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THE UNIVERSITY OF ALBERTA

A Study of the Process Parameters of a Continuous Contactor for Osmotic Treatment

by

Hong Qi (C)

A THESIS

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **A STUDY OF THE PROCESS PARAMETERS OF A CONTINUOUS CONTACTOR FOR OSMOTIC TREATMENT** submitted by **Hong Qi** in partial fulfillment of the requirements for the degree of **Master of Science in Food Engineering.**

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(supervisor)

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DATE: June 9., 1989...

ABSTRACT

Osmotic dehydration has been suggested as a way to remove water from fruits and vegetables before conventional drying or freezing, to reduce energy consumption and improve product quality. In this study, a pilot-scale belt-type osmotic contactor was designed and used in a continuous osmotic dehydration process in order to get maximum water removal from fresh fruits and vegetables with a minimum contact time. The carrot was chosen as a representive vegetable and the osmotic solution used was a sucrose/sodium chloride/water ternary mixture with a total solids concentration of about 50 to 55% (w/w). The optimum condition from the experiments was found with 44% sucrose/7% NaCl aqueous solution at 16 minutes contact time, resulting in a 26% water loss and the highest ratio of water loss over solids gain. The mass and water reduction, sugar and salt gain were fitted with exponential functions with respect to time.

The phenomenological approach accurately described the non-linear relationship between the fluxes and thermodynamic forces. Based on this, a model for the prediction of mass changes, taking into account the cellular structure shrinkage during the process, was developed with the assumption of constant concentration on the solution side. Using the model, the parameters are well predicted.

The model optimizes the performance of the osmotic contactor by determining the best parameters for the removal of water from the carrot cubes to a desired final characteristics. Alternation with different

concentrations of osmotic solutions in each section did not show osmotic effectiveness, especially when the process began with high salt concentration in the osmotic solution.

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LIST OF SYMBOLS

a	side length of carrot cube (m)
a_{ij}	coefficients of multi-linear regression
a_w	water activity
A	surface area (m^2)
A	parameter in curve fitting
B	parameter in curve fitting
C	parameter in curve fitting
D	diffusion coefficient (m^2/s)
DF	dilution factor
F	Faraday's constant
h	step increment (s)
K_{ij}	mass transfer coefficient
J_i	i-th generalized flux (kg m^{-2} s^{-1})
J_i'	i-th generalized reduced flux (dimensionless)
$J_{i,max}$	i-th maximum generalized flux
L_{ij}	i, j-th generalized phenomenological coefficients ($K\ kg^2\ J^{-2}\ m^{-2}\ s^{-2}$)
m_{cube}	mass of a single carrot cube (kg)
m_{sc}	molality of sodium chloride
M	mass of carrots (kg)
M_i	mass of species i (kg)
ML	mass loss (%)
MSC	molecular weight of sodium chloride
MSU	molecular weight of sucrose

MW	molecular weight of water (kg $kgmol^{-1}$)
n	number of cubes
NSC	normalized solid content
PA	peak area
ΔP	hydrostatic pressure difference (Nm^{-2})
R	universe gas constant (J $kgmol^{-1}$ K^{-1})
R	ratio of salt over sugar in solution
SCC	sodium chloride content (%)
SCG	sodium chloride gain (%)
SUC	sucrose content (%)
SUG	sucrose gain (%)
T	absolute temperature (K)
t	time (s, or min)
TS	total solids (%)
Vc	volume of carrot cubes (m^3)
V	partial specific volume (m^3 kg^{-1})
V_j	partial molar volume of species j (m^3 $kgmol^{-1}$)
W_i	wight fraction of species i
WL	water loss (%)
x_i	mole fraction of species i
X_i	difference in chemical potential of component i divided by temperature
Y_j	j-th generalized thermodynamic forces [J K^{-1} m^{-1} (units of quantity transferred)$^{-1}$]
Z	direction of diffusion (m)
Z_j	electrical charge of species j

Greek Letters

γ	activity coefficient
θ	time
μ_i	chemical potential of species i (J kg^{-1})
$\Delta\mu_i$	chemical potential gradient of species i (J kg^{-1})
ρ_c	density of carrots (kg m^{-3})
ρ_b	bulk density of the bed of carrot cubes (kg m^{-3})
$\Delta\phi$	electrical potential difference (volts)

Superscripts

c	quantity related to carrots
cor	corrected quantity
eq	equivalent quantity
exp	experimental quantity
in	quantity related to the inside of the cellar volume
out	quantity related to the extracellalar volume
pre	predicted quantity
s	a quantity related to the osmotic medium
o	an initial quantity
∞	a quantity at equilibrium

Subscripts

c	carrot
d	dish
in	insoluble solids

i,j,k	species
m	mass
o	initial quantity
sc	sodium chloride
ss	soluble solids
su	sucrose
ts	total solids
w	water

1 INTRODUCTION

Removal of water by osmosis from biological materials has drawn increasing attention as a potential alternative or supplementary operation to conventional drying or freezing processes in recent years (Ponting *et al.*, 1966; Farkas and Lazar, 1969; Ponting, 1973; Hawkes and Flink, 1978; Maltini and Torreggiani, 1981). Although air drying and freezing are the most commonly used preservation methods for fruits and vegetables, these processes may considerably reduce the quality of the products in terms of rehydration ability, color, texture and flavour and are associated with high cost. Attempts have also been made to remove water from products by immersing the material in a suitable solution, a process known as osmotic dehydration.

Osmotic dehydration of fruits and vegetables is possible because cell membranes are semi-permeable and thus allow water to pass through more readily than solutes. The different aspects of osmotic dehydration such as the choice of solutes and their concentrations (Hawkes and Flink, 1978; Flink, 1980), temperature (Lerici *et al.*, 1985; Ponting *et al.*, 1966), time (Farkas and Lazar, 1969), and the quality of the final product (Ponting, 1973; Dixon and Jen, 1970) have been investigated.

It has been recognized, in general, that the water loss in osmosed materials is increased by increasing the solute concentration, immersion time, temperature, and agitation.

The advantages of osmotic dehydration in comparison with other drying processes are: minimized heat damage, less discoloration of fruit (Ponting *et al.*, 1966; Contreras and Smyrl, 1981); increased retention

of volatile and pigments (Flink and Karel, 1970); improved textural quality (Shipman *et al.*, 1972); reduced water load in subsequent processes and improved process economics (Hawkes and Flink, 1978) and lower operation costs by removal of water without going through a phase change.

However, most of the studies have been limited to laboratory scale which is hard to scale up for commercial applications. One major concern of commercial operation is the efficiency and feasibility of an osmotic process. The first investigation of the osmotic process in a pilot-plant batch system demonstrated the operational problems of commercial osmotic dehydration (Farkas and Lazar, 1969). Although the recent successful study of a pilot-plant batch system (Genneugues, 1986) reveals the possibility of further application of the process. Previous study fails to provide the information on a continuous process which might be considered as the most efficient way of minimizing operational costs (Schwartzberg, 1980).

The process of osmotic dehydration of plant materials involves simultaneous water removal and solutes uptake. The internal resistance of transport of any component due to diffusional flow is a controlling step (Magee *et al.*, 1983).

Most of the diffusional mass transfer studies of food systems deal with either a binary system (Fick's law description) (Conway *et al.*, 1983; Soddu & Gioia, 1979) or assume independence of the movement of each species in a multicomponent system (Pflug *et al.*, 1967; Menting *et al.*, 1970). However, they fail to give accurate estimation due to the exclusion of the interaction between the components.

An alternative approach to modeling a multicomponent mass transfer process is based on irreversible thermodynamics, taking into account the fluxes of the different components of the system and the interactions between the different components for a pilot scale batch system (Guenneugues 1986). Unfortunately, his model was empirical and the application to other systems is impossible.

This study contributes to the investigation of the osmotic behavior of carrot tissue in a continuous osmotic contactor and optimize the processing parameters. For this purpose, the study was directed toward the following specific objectives:

1). To design and construct a pilot scale osmotic contactor which provides continuous operation, and conduct preliminary study to obtain appropriate operation conditions.

2). To determine the osmotic behavior of carrot cubes both with this unit and under equilibrium conditions.

3). To develop a mathematical model for the prediction of mass changes, taking into account the cellular structure damage during the process. Validation of the model is done by comparing the experimental sucrose, NaCl and water concentration with those predicted.

4). To conduct a parametric study of the continuous osmotic contactor and to optimize the operational conditions.

2 OSMOTIC TREATMENT: A REVIEW

In this review, the principle of osmotic treatment will be defined. The general application of osmotic treatment in the food area will be presented with a special emphasis on fruit and vegetable processing, as well as final product qualities. Important parameters in the osmotic process such as the composition and concentration of osmotic solutions, temperature and contact time will be discussed. The general behavior of tissue upon osmosis and basic unit operations or similar processes will be reviewed. Finally, the chapter will conclude with an outline of existing models and the application of the phenomenological approach to this process.

2.1 Principle of Osmotic Treatment

The osmotic pressures developed across membranes were observed centuries ago (Katchalsky, 1967). In general, if there is a solution on one side of a membrane permeable to water only and another solution of a different concentration on the other side, osmosis will occur. The water will diffuse from the side with the less-concentrated solution to the side with the more-concentrated solution, until the water chemical potential on both sides is equal, and equilibrium is reached.

Extensive studies of the application of osmosis have been made in chemical and biological fields. The application of osmotic dehydration for fruits and vegetables was initiated by Ponting *et al.* (1966).

Osmotic treatment is a water removal process based on the water and

solute activity gradients across a cell's semi-permeable membrane. This water removal process is possible due to the selectivity of the semi-permeable cell membrane which allows water to pass through readily, but acts as a barrier for some solutes. When immersing plant materials in an aqueous solution, two major counter-current flows will take place simultaneously. One is the water flow from the biological structure to the osmotic medium and the other is the flow of solutes from the osmotic medium to the plant material. There is also a small migration of soluble solutes from the plant tissue to the osmotic medium such as organic acids, minerals and vitamins (as shown in Fig 2.1). Thus osmotic treatment is a dynamic process in which water removal is very rapid at the beginning, due to large differences in chemical potential, and then slows down during the later stage of the process.

2.2 Applications of Osmotic Treatment in the Food Area

Water plays a predominant role in the physical, chemical and microbiological properties of foods. Most unit operations in food processing have used removal of water to stabilize the material, such as in drying, concentration, transfer into a nonactive component such as in freezing, or immobilization in gels, structured foods, or low and intermediate moisture foods (Le Maguer, 1987).

Air drying and freezing are the most commonly used preservation methods for extending the storage life of fruits and vegetables. It makes these foodstuffs available for supply not only during a relatively short harvesting period but also throughout the year. However, these

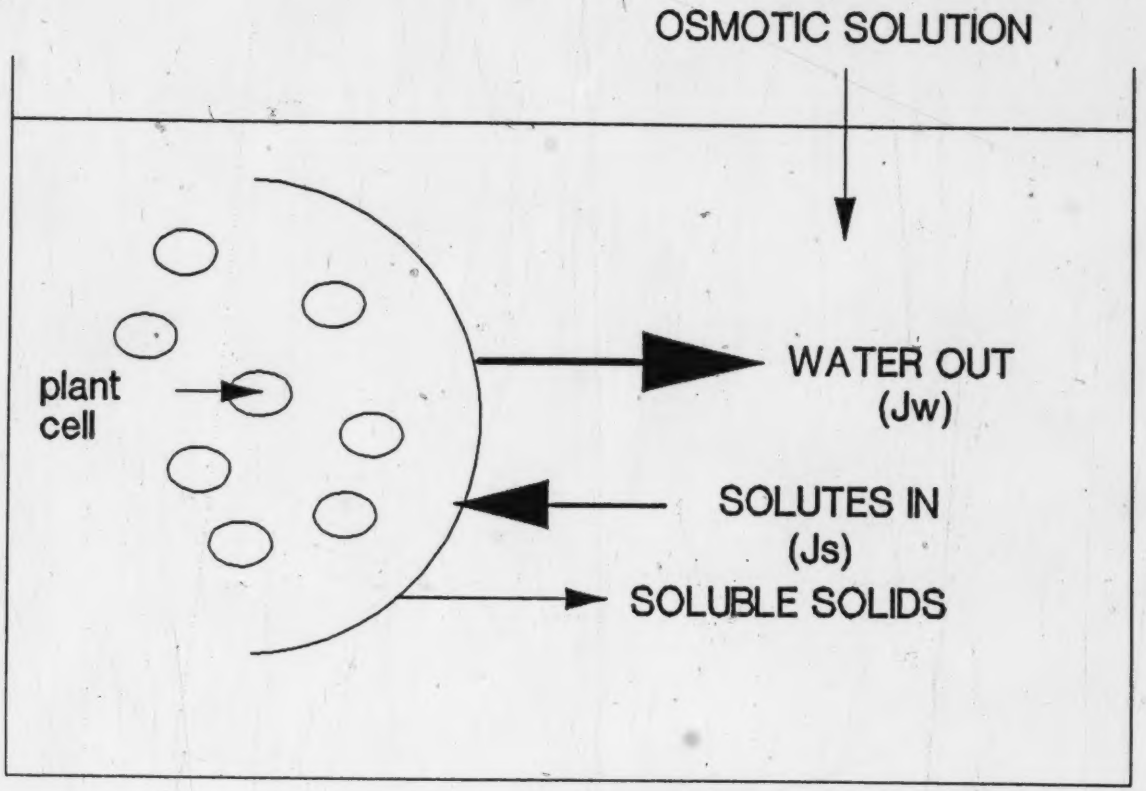

Fig. 2.1 Fluxes Involved in an Osmotic Treatment

processes are energy-intensive. They also considerably reduce the quality of the products, and are responsible for the initiation of many undesirable changes. Reduction in nutrient content always occurs in drying and freezing. The most common quality defects of dehydrated food are tough texture, slow or incomplete rehydration, and loss of juiciness, as well as unfavorable changes in color and flavor (Karel 1975).

It is generally known that the highest quality of dried products is achieved by freeze drying, but this technique is one of the most expensive. The large amount of energy spent in the freezing process includes the energy spent in freezing, packaging, transportation and storage of fresh fruits and vegetables with a large amount of water present in them. With higher costs of energy and other resources, there is an increasing concern for the high cost of these unit operations. New dehydration or water removal processes and important modifications of current techniques are being developed. An interesting technique is the use of a solvent to extract part of the moisture from products by osmosis, known as osmotic treatment, before they are dried or frozen. Since the water removed does not go through the phase change, the energy requirement is minimized and the overall energy consumption is reduced.

In recent years, the osmotic process has drawn great interest from industry due to the possibility of developing a new way of preservation, or as a pre-treatment before conventional processes to improve quality of final products and reduce the cost. Many authors have suggested applying the osmotic treatment as an intermediate step prior to drying and freezing to reduce product water load to the dryer or freezer and

improve product quality (Ponting *et al.*, 1966; Farkas and Lazar, 1969; Hawkes and Flink, 1978; Contreras and Smyrl, 1981; Islam and Flink, 1982; Bolin *et al.*, 1983; Lenart and Flink, 1984a, 1984b). These studies have evaluated the influence of process variables such as types of solutes, concentration, processing temperature, contact time and recycling of osmotic solution on the subsequent drying or freezing behavior of food materials, the characteristics of final products and sensory evaluations. There is also a potential application for producing intermediate moisture food using osmosis techniques (Maltini and Torreggiani, 1981). The application of osmotic treatment for food processes is shown in Fig. 2.2.

2.2.1 Intermediate Moisture Food (I.M.F)

Numerous studies have focused on the importance of water activity in relation to food stability (Troller and Christian, 1978). The effects of water activity on microbial growth, chemical reactions and enzyme activity have also been studied extensively (Troller and Christian, 1978; Karel, 1975).

In recent years, a new technique in the food industry is based on the principle that added solute lowers the availability of water by binding it and making it chemically and biologically unavailable. This has been used to obtain shelf-stable products with a water activity(a_w) between 0.65 to 0.90, and a water content generally in the range of 20 to 50% (Maltini and Torreggiani, 1981).

The reason why food with an intermediate moisture is preferred to

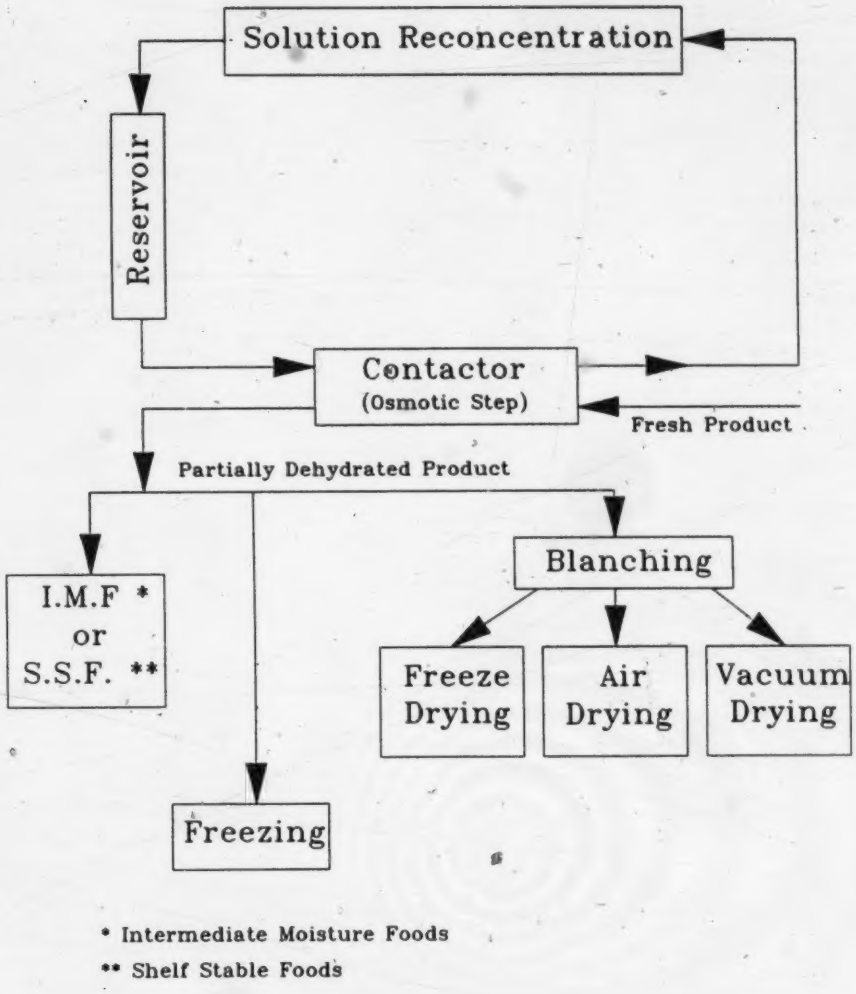

Fig. 2.2 Diagram of Methods Using an Osmotic Step for Food Processes

dry foods is that people like food to be in a moist and tender state for mastication. The initial use of this technology was in the area of pet foods. After successful application in the US military, the National Aeronautics and Space Administration more recently, the application of I.M.F has been developed for general human comsumption.

The basic working principles behind I.M.F are lowering water activity by adding solutes, such as polyhydric alcohols, sugars or salt, and retarding microbial growth by adding antimicrobial agents, primarily antimycotic agents such as propylene glycol and sorbic acid.
Intermediate moisture foods (I.M.F) have increased in popularity because these foods offer a combination of shelf stability and convenience.

A number of authors have investigated the formation and processing of I.M.F (Bone, 1973; Ross, 1975), the water binding properties of different kinds of compounds (Sloan and Labuza, 1976), and a model for calculating water activity for mixed solutions (Bone et al, 1979).

Intermediate moisture products have been produced by immersing fruit into a 70°Brix sucrose solution to reduce weight by fifty percent (Ponting *et al.*, 1966; Moy *et al.*, 1978).

Karel (1975) also stated that osmotic drying is a technique in which simultaneous removal of water and incorporation of solutes was obtained. The potential for applying osmotic treatment to produce intermediate moisture food has been investigated by Maltini and Torreggiani (1981). They proposed osmotic treatments to produce shelf-life-stable products with a water content in the range of 65-75% and a_w between 0.94 and 0.97. After vacuum packaging and pasteurization, the products remained stable for many months at ambient

temperature without further stabilizing treatments. As the popularity of piece form and fresh-like fruits and vegetables is increasing considerably, this technique appears to be of great interest because it combines low processing cost and high quality characteristics. The important fact is that fruits or vegetables are never submitted to heat treatment and the extent of dehydration is reduced so that no morphological changes occur in the tissue.

2.2.2 Intermediate Step Prior to Drying and Freezing

One of the energy-efficient methods for removing moisture from a food piece is by osmosis. Numerous studies have applied osmotic treatments as an intermediate step in air drying, vacuum drying and freeze-drying. (Ponting *et al.*, 1966; Farkas & Lazar, 1969; Ponting, 1973; Lerici et al, 1985; Hawkes & Flink, 1978; Flink, 1980). The main advantage of this treatment is that it reduces the water load in subsequent processes significantly, and improves process economics so that the overall energy cost is reduced.

Ponting *et al.* (1966) first proposed a process for a reduction in weight of 50% for apples by osmotic dehydration, after which the apple was dried in an air or vacuum dryer. These dehydrated products were suitable for consumption directly in the dry state. Partial drying by osmosis in sugar or syrup is especially suitable for further vacuum drying, with good color, texture and moisture content equivalent to those obtained by freeze drying.

Lerici *et al.* (1985) evaluated the influence of temperature, sugar

concentration and system agitation on the freeze drying behavior of apple slices. They indicated that the freeze drying time for the osmotically treated samples was reduced by about 15%. Flink (1980) reported that osmotic concentration can be used as a pre-step to freeze drying to reduce drying time as well.

Kim and Toledo (1987) compared osmotically dehydrated blueberries followed by high temperature fluid bed conditions with nontreated ones. The former ones are soft, had a raisin-like texture and would be suitable for consumption in the dry state.

Water removal from materials before freezing has been studied extensively. However all these studies considered air drying as a means of partial dehydration before freezing, for vacuum drying or freeze drying are considered too costly to use as a means of water removal. Osmotic dehydration may be a good alternative to this dehydrofreezing process. In osmotic dehydration, about 50% of the product weight is removed prior to freezing, yielding a concentrated product and thus reducing the energy cost during freezing.

Le Maguer and Biswal (1984) proposed low temperature osmotic dehydration using an aqueous solution of sodium chloride and ethanol called the dehydrocooling process, which would simultaneously cool and remove water from vegetables before freezing. Because the products are cooled through the removal of sensible heat only, a saving in the latent heat of fusion for the amount of water removed from the products is obtained.

2.2.3 Characteristics and Economic Aspects of the Products

High quality osmotically dried fruits in terms of color and flavor have been obtained with little or no use of sulfur dioxide (Ponting *et al.*, 1966). The moisture content is easily reduced to about 6% for apples that have been osmotically dehydrated followed by air drying. Fruits which have been partially dried by osmosis in sugar or syrup are especially suitable for further vacuum drying in terms of color and the moisture content can be rapidly reduced to a level that could be obtained only by freeze drying. Natural flavor and a crisp honeycomb-like texture makes vacuum dried fruits excellent for snack items. Because of the low temperature of osmotic dehydration combined with the protective effect of sugar, the flavor and color of peaches remain fresh and natural, and the taste was very much like the fresh fruits. Furthermore Ponting (1973) reported that osmotically vacuum dried fruits are very stable in storage. Most of them retain their good quality for at least a year at room temperature and three years at $1^{o}C$. The process prevented enzymatic browning, but increased the sugar content and intensified the sweetness of the processed fruit (Farkas and Lazar, 1969; Dixon and Jen, 1977), and increased the sugar to acid ratio (Dixon and Jen, 1977). Osmotic dehydration increased nutrient retention during subsequent air drying, resulted in a two to five fold increase in product output in a 45% sucrose /15% salt solution for potatoes (Islam and Flink, 1982), and minimized the color and flavor change caused by heat damage.

Curry *et al.* (1976) found that the incorporation of 0.2 M NaCl into freeze-dried carrot slices brought a 54% increase in the rehydration

ratio over nontreated samples. The osmotic dehydration step stabilizes the pigments of carrots against oxidation and promotes the retention of carotenoid pigments in freeze dried carrots which had been treated with a salt/sucrose mixture prior to freeze drying, while untreated samples rapidly lose their orange color. Osmotically freeze dried samples have remained virtually unchanged in color after up to 2 years of storage (Flink, 1980).

Islam and Flink (1982) presented the results of osmotically concentrated potato followed by solar drying. An improved appearance and texture have been achieved compared to plain solar-dried products. The osmosed samples were much whiter than the plain solar-dried samples which always have to be improved by blanching or sulfiting. Organoleptic evaluation also indicated a high level of acceptability of the osmotically solar-dried product, while retention of ascorbic acid was comparable to that found in other dehydration processes reported in the literature.

Yang *et al.* (1987) also investigated a combination process of osmotic dehydration and freeze-drying to produce a raisin-type blueberry product which had good texture, flavor, overall acceptability, and a predicted shelf-life of 16 and 64 months at a storage temperature of 25°C and 5°C respectively.

Moreover, osmotic syrup can be reconcentrated and reused for osmotic water removal through at least five complete cycles without adversely affecting the fruit being processed (Bolin *et al.*, 1983). This makes the osmotic process economically and commercially feasible.

2.3 Important Parameters of the Osmotic Process

Numerous studies have investigated the effect of different osmotic agents, concentrations, temperature, agitation, recycling of osmotic media, contact surface area to weight ratio of plant material, the properties of plant materials and the characteristics of the final product quality. (Ponting *et al.*, 1966; Farkas and Lazar, 1969; Ponting, 1973; Karel, 1975; Cipolletti *et al.*, 1977; Lerici *et al.*, 1985; Hawkes and Flink, 1978; Contreras and Smyrl, 1981; Andreotti *et al.*, 1983; Conway *et al.*, 1983; Lenart and Flink, 1984a).

2.3.1 Composition and Concentration of Osmotic Solutions

The choice of solute and the concentration depend on several factors. Two of the most important factors which control the choice of osmotic agents are the organoleptic properties of the final products and the cost of solutes. The capacity of a compound to lower water activity will also influence the driving force for mass transport. Since the maximum concentration of a compound depends on its solubility, it will consequently affect the driving force for mass transport as well. It is also not desirable to have a solute that can react with the final products. Availability of solutes, and permeability of cell membrane to particular compounds resulting in solutes uptake should also be taken into account. Among other things, the choice of solute depends on the extent to which the solute infusion and water loss helps in preservation of the products.

Bolin *et al.* (1983) found that the higher diffusivity of high fructose corn syrup (HFCS) resulted in a faster rate of penetration into fruit pieces than sucrose solutions. From an organoleptic evaluation point of view, sucrose is preferred as an osmotic medium to HFCS.

Contreras and Smyrl (1981) reported that the use of corn syrup resulted in a 70% weight reduction of apple rings and the products are visually, textually and organoleptically acceptable. They also suggested that corn syrup solids (dextrose equivalent 28) result in less solid gain (1.80 g/100 g initial apple) in apple rings using 42% solids corn syrup after 4 hour immersion, compared with a solid gain of 13.32g /100g initial apple using 40% sucrose reported by Hawkes and Flink (1978).

Besides producing an acceptable product of low sweetness, the use of corn syrup solids may be advantageous for subsequent processes such as freeze-drying and vacuum drying. As Menting *et al.* (1970) outlined, water diffusion coefficients are extremely sensitive to dissolved solids; the diffusion coefficients decrease when the solids content increases. Thus a low solid uptake during the concentration step could allow for a more rapid drying step.

Lactose and maltodextrin have been proposed as substitutes for sucrose to reduce sweetness and cost. The limitation of solubility of lactose becomes a potential problem (around 25%) in application as an osmotic agent. Even in dry lactose, a caked region forms around a fruit slice giving a low water permeability and preventing further transport of water from the fruit slice. It appears that pure lactose is not a promising osmotic agent (Hawkes and Flink, 1978). A lactose and sucrose

mixture would result in higher solids content. Hawkes and Flink(1978) reported that maltodextrin can be used as an osmotic agent at a higher total solids concentration, or in mixed systems.

It is reported that calcium chloride as an osmotic agent has a firmness effect on the texture of apples as well as a synergistic effect with ascorbic acid or sulfur dioxide in preventing browning (Ponting, 1973). However, the amount of calcium chloride should be limited, due to an imparted bitterness.

Moy *et al.* (1978) investigated the effect of combining organic acids and sucrose in the dehydration of papaya and mango, and showed that acidification increased the rate of water removal for papaya. This was due to the change in tissue properties (reversal of pectin gelation) and not from the increase in solute concentration, since acids were added at concentrations (1-4.0%) which were low in comparison to sucrose concentration (60%).

Ethanol has been used by Le Maguer and Biswal (1984) to decrease the viscosity and the freezing point of an osmotic solution (ethanol - sodium chloride - water system) in a dehydrocooling process. However, organoleptic evaluation of the carrot slices revealed that the use of ethanol produces a slight medicinal aftertaste. Predipping in a sucrose solution followed by freezing in the aqueous freezant 15% sodium chloride and 15% ethanol gave satisfactory results.

Cipolletti *et al.* (1977) suggested that compounds such as sucrose, lactose etc... are not suitable as freezants due to an excessive increase in viscosity at low temperatures.

Among all these osmotic agents, concentrated sucrose solutions

(50-70% Brix) have been the most commonly used, while sodium chloride is a particularly effective osmotic agent for vegetables.

Sucrose

Sucrose has been found to be one of the best osmotic agents because of its effectiveness, convenience, and desirable flavor.

As Ponting (1973) pointed out, there are two advantages of a sugar solution in producing a high quality product. First, it is a very effective inhibitor of polyphenol oxidase, and secondly it prevents the loss of volatile flavouring constituents during dehydration. A similar conclusion has been obtained by a number of authors (Farkas and Lazar, 1969; Flink and Karel, 1970; Flink, 1980). According to Flink and Karel (1970), carbohydrates promote retention of volatiles. The use of a sucrose solution as a barrier to the entrance of oxygen, with consequent reduction in enzymatic browning, has been observed by Karel (1975). In addition, sucrose has a relatively low cost . The excellent osmotic ability of sucrose solution is due to the cell membrane impermeability to it, and to the fact that the diffusivity of sucrose is much lower than that of water. As a consequence, the transmembrane transport is simply the flux of water through the membrane. The driving force of the flux is proportional to the chemical potential of water. Sucrose osmosis appears to approach equilibrium primarily by removal of water from tissue with only little solids uptake. One of the limitations in its application to vegetable processing is the sweetness of sucrose.

Sodium Chloride

Sloan and Labuza (1976) stated that particular components, such as salt or glycerol, are particularly effective in reducing water activity, or conversely give higher moisture contents for a specific water activity level. This capability of lowering water activity, resulting in a high driving force in mass transport, makes sodium chloride solution an excellent osmotic agent. It leads in a fast rate of water removal and a higher allowable moisture content for the final dried products. Hawkes and Flink (1978) reported that 25% sodium chloride is the best osmotic agent so far in terms of its ability to lower a_w, and increase driving force of water removal. Lenart and Flink (1984b) noted that the driving force for salt is much larger compared to sucrose for the same level of concentration. Furthermore, a higher degree of reconstitution of air-dried carrots with pretreatment in 10% sodium chloride has been observed by Speck (1977).

It is also a common method to immerse cut fruits in dilute sodium chloride solution (1% to 3%) prior to freezing to prevent enzymatic browning. Polyphenoloxidases are inhibited by chloride ions according to Fennema (1975).

The incorporation of sodium chloride into freeze-dried carrot slices was found to have a marked effect on rehydration (Curry *et al.*, 1976). After 5 min of rehydration, the 0.2 M sodium chloride treatment resulted in a 54% increase in rehydration ratio over nontreated control samples.

Recently, Lewicki *et al.* (1984) conducted the kinetic study of mass

transfer of sodium chloride occurring in potato tissue during osmotic dehydration. They reported that with a 15% sodium chloride solution, sodium chloride penetrates into potato tissue to a considerable depth (4 to 18 mm) within the temperature range of 20°C to 40°C and contact time from 1 to 21 hours. The coefficient of diffusion of sodium chloride depends on concentration and temperature. The osmotic dehydration of potato takes place most effectively at a temperature of 30°C within one hour.

Because of the penetration of sodium chloride, the amount to be used must be limited due to saltiness, especially in the case of fruit dehydration. From the organoleptic point of view, in order to achieve satisfactory results the concentration of sodium chloride in the osmotic solution should be around 10% - 15%. But as the penetration is time dependent, it is possible to design a process by optimizing the processing parameters achieving both economical and organoleptically desired results.

Combinations of sucrose and sodium chloride

Many authors have evaluated the effectiveness of combined solutes in osmotic solutions in order to obtain optimum values, that is maximum water loss and minimum solute gain with good organoleptic qualities and a low cost.

Lenart and Flink (1984b) discussed that at 60% total solids level, sucrose/salt mixtures are the most effective solutions giving a comparatively low level of water activity compared with 60% sucrose

solution alone which may be attributed to the higher molar concentration of the sucrose/salt solution.

Flink (1980) investigated the influence of osmotic concentration on the drying behavior and product quality of carrot slices using a salt-sugar mixture. Tests of combinations of 20, 40 and 60% sucrose with 5, 10 and 15% salt were evaluated with respect to taste and texture of raw and cooked carrot slices. It was found both 40% sucrose/ 5% salt and 40% sucrose/10% salt were desirable.

Osmotic concentration in a salt/sugar solution prior to drying resulted in an increased solids density due to solids uptake in osmosis (Islam and Flink, 1982). It also reduced the water load to the dryer and consequently increased the capacity of the equipment and produced a higher, allowable moisture content for final products from the dryer due to the influence of salt uptake on the water sorption behavior of the products (Mazza 1983).

According to Lenart and Flink (1984b), the water removal effect with sucrose/salt mixtures at sucrose concentrations above 40% is as high as that with 60% sucrose alone, since the high sucrose concentration forms a compacted surface layer which limits interior water removal. There is a much higher driving force in an osmosis with a 45% sucrose/15% salt solution (a_w =0.691) than with a 60 % sucrose osmosis solution (a_w = 0.899). Furthermore, with the addition of salt to the osmotic medium, the formation of the compacted surface layer can be hindered, and salt can penetrate to the interior of the sample to lower the interior water activity effectively, thus increasing the allowable moisture content of final products at the same a_w level and

extending the shelf life of the products.

So, in a mixed system of sucrose and sodium chloride, sucrose having a high molecular weight cannot easily diffuse through the cell membrane, thus resulting in high concentration gradients, i.e. high driving force. The approach to osmotic equilibrium of the system is primarily by flow of water from the tissue. Sodium chloride can more easily penetrate into tissue resulting in water loss as well as solids gain. Salt solution also hinders the shrinkage at the surface layer occurring mostly with sucrose solution. Therefore the combination of the two creates a high molar concentration, gives a high level of water loss, and produces high solids content prior to subsequent processes. The blend also lowers the cost of osmotic media compared to pure sucrose. In addition, the blend may have some taste advantages over a pure sucrose medium. The optimum level combination depends on the requirements of the final products and additional preservation functions.

2.3.2 Temperature

In general, the rate of water loss is increased with the increase of temperature. However, there is a limit, around 50°C to 60°C, above which enzymatic browning and flavor deterioration begin to take place (Ponting *et al.*, 1966), and the cell membranes are destroyed. Lewicki *et al.* (1984) reported that osmotic dehydration takes place most effectively at a temperature of 30°C in a sodium chloride solution within one hour.

2.3.3 Agitation

The rate of osmotic dehydration is considerably faster in a sugar solution with agitation than without agitation (Ponting et al ., 1966). The influence of agitation on the mass transport coefficients was investigated by Hawkes and Flink (1978). It was found that agitation had little effect with a low concentration of osmotic solution. However, as the solution concentration increases, the viscosity and resistance to mass transfer increase. Thus an agitated system has a higher external mass transport coefficient compared with a non-agitated system.

2.3.4 Contact Time

In general, an increase of contact time increases weight loss and water loss (Ponting *et al.*, 1966; Farkas and Lazar, 1969).

Fig. 2.3 shows schematically how the relationship of water and solutes content changes with respect to time when fruit pieces are exposed to concentrated osmotic solutions. Although the water loss increases as a function of the immersing time, the rate of water loss which is the tangent to the curve decreases. The rates of water loss and solutes uptake as well as the difference between these two rates are maximum at the beginning.

Several of the principal soluble constituents of an apple, such as organic acids, reducing sugar, minerals and nitrogen components, undergo

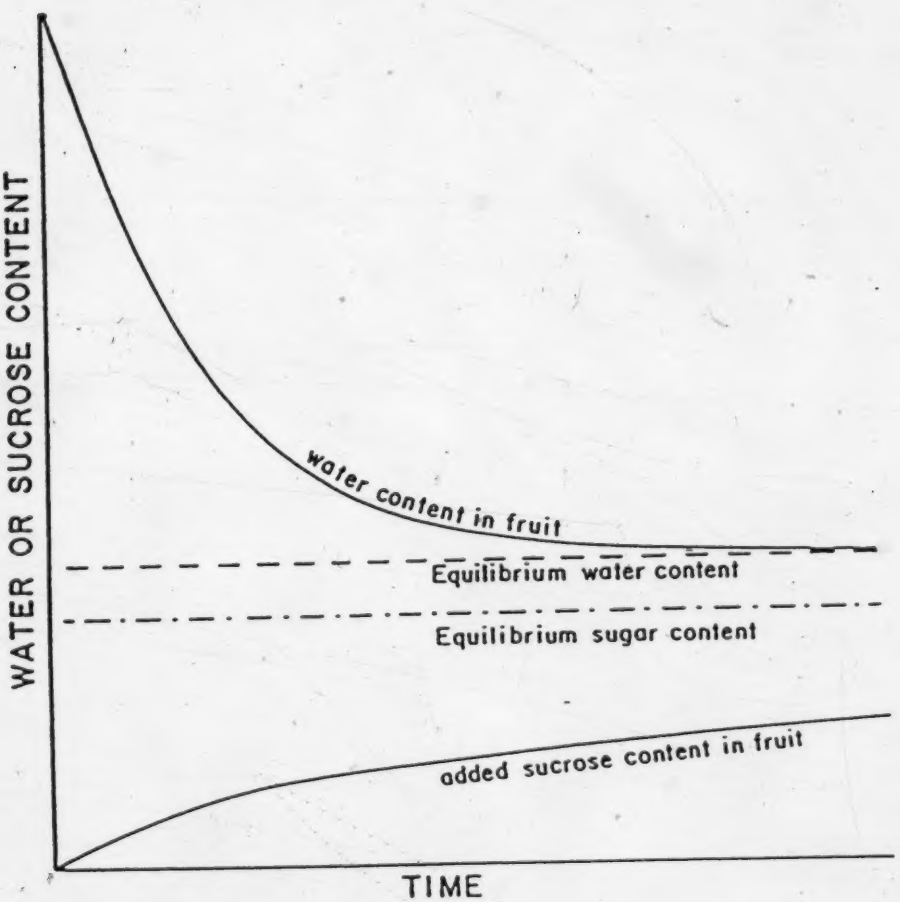

Fig. 2.3. Approach to Equilibrium Water and Sugar Contents during Osmotic Drying Karel(1975)

a considerable change during osmotic dehydration (Lerici *et al.*, 1985). In the first 2 hours, water diffuses out of the apple with little or no loss of the soluble constituents. However, after a 2 hour immersion, appreciable amounts of these substances started to diffuse out of the apple slices.

According to Hawkes and Flink (1978); Giangiacomo *et al.* (1986); Torreggiani *et al.* (1987), the maximum mass exchange takes place within the first two hours of osmotic treatment. It is obvious that if the process is interrupted early on, a large amount of water can be removed without much solutes uptake (Karel, 1975). However, if the process time is too long, there is considerable diffusion of solutes such as sodium chloride or low molecular weight compounds into the fruits or vegetables. It is thus particularly important in the design of a continuous contactor to keep the contact time as short as possible in order to get a maximum ratio of water loss to solutes uptake.

2.3.5 Pretreatments

It has been generally recognized that some of pretreatments such as blanching or freezing and thawing are detrimental to the osmotic process. Osmotic dehydration is possible due to the selective permeability of the cell membranes. Any process which disrupts the cell membrane will result in undesired osmotic results.

Peri *et al.* (1975) applied a pre-treatment by dipping whole grapes in an ethyloleate alkaline solution, which was found to increase the kinetics of air drying. The dipping caused a solubilization of the waxy

coating of the grapes and modified the permeability of skin without damaging the internal structure. A very slow transfer of solutes was found. It was stated that the skin of grapes acts as a selective semipermeable barrier.

Camirand *et al.* (1968) developed the concepts of membrane cast such as calcium pectate around the food to be dehydrated. The presence of the membrane prevented uptakes of solutes by food materials, but allowed removal of water minimizing the solute uptake. Good results have been obtained with some foodstuffs such as fish and meat. However, this coating technique was no more efficient than normal osmotic dehydration.

2.3.6 Nature of the Materials

The properties of plant materials have a great influence on osmosis (Ponting, 1973). Apparently, the total solid content seems to be a crucial factor for the materials to be osmotically dehydrated.

Tomatoes and citrus fruits are poorly suited to osmotic dehydration because of the excessive loss of juice, but apples and bananas are very good subjects for osmotic dehydration.

The textural differences of tissues following immersion in either sugar or salt solutions has been reported in the literature. Lenart and Flink (1984b) stated that the eventual effect of cellular dehydration on transport properties will depend on tissue properties, especially the intercellular space present in the tissue and the amount of the insoluble solids.

Moy *et al.* (1978) showed that a combination of sucrose and acid

increased the osmotic dehydration rate and water removal from papaya, by inhibiting gelation. But this was not the case with mango.

Under the same osmotic conditions, cherries and peaches behaved differently, illustrating the intrinsic properties of these two fruits such as the structure and compactness of the tissue (Giangiacomo *et al.*, 1986). The exchange between the syrup and fruit during osmotic dehydration is not only related to the diffusion but also involves the original sugar in the fruit and enzymatic activity.

2.3.7 Basic Tissue Behavior upon Osmosis

Most studies have focused on the effects of different types of solutes associated with solids uptake and water loss of plant materials as a whole.

The mass transport phenomenon occurring in plant tissue upon osmosis involves complex mechanisms. The physical properties of plant materials have great effects on tissue behavior upon osmosis.

More recently, Marcotte (1988) pointed out three possible pathways that solute or solvents may follow in the tissue that are considered responsible for the behavior of the plant material upon osmosis. They are the apoplast, plasmodesmata and transmembrane transport.

The apoplast is a diffusion of molecules in the cell wall and the intercellular space between cells. The plasmodesmata is characterized by a movement of molecules from one cell to another through small channels, and transmembrane transport is an exchange between protoplast and intercellular space.

In the equilibrium study of potato tissue in a sucrose solution, a constant total final volume was found for a wide range of concentrations (10% to 40%) of sucrose solutions by Marcotte (1988). It was found that the extracellular space increases as soon as incipient plasmolysis is reached, because the sucrose and water enter the extracellular space preventing the cell structure from collapsing. There is also no penetration of sucrose in the cellular volume. The mass transport phenomena was influenced by the shrinkage of the products leading to decreased surface area for mass transfer.

Detailed information on transport phenomena within tissue or cell may be found in Marcotte (1988).

2.4 Basic Unit Operations

Attempts have been made to understand the mass transfer phenomena of plant materials during an osmotic process and relate it to comparable unit operations. One of the well-known and widely-used unit operations in chemical and food industries is leaching.

Leaching is an unit operation aimed at the selective removal of soluble components from a solid matrix in a solvent phase (Spaninks, 1979). In some cases, a desired product can be recovered; in other cases, it removes unwanted constituents or contaminants. Examples of the leaching process include: extracting sugar from sugar beets, desalting pickles, removing caffeine from coffee beans, etc. An extensive list of examples of commercial importance can be found in Schwarzberg (1980).

2.4.1 Batch Operation

In batch leaching, the solids and extracting solvent are loaded into a vessel. The mixture is allowed to sit for a while with or without stirring, and then the liquid and solids are separated (Schwartzberg, 1980). Industrially, such systems are used to infuse salt into and diffuse sugars out of cucumbers, olives, and shredded cabbage or vice versa.

Most current work in osmotic studies utilizes the batch leaching concept. Farkas and Lazar (1969) first initiated the study of feasibility in preparing non-sulfured dehydrofrozen pie stock from apples by osmotic drying in a pilot plant batch study. The equipment used in the pilot plant test is shown schematically in Fig. 2.4. This study demonstrated the potential design and operating problems of commercial osmotic dehydration (Farkas and Lazar, 1969).

A major problem of the test was the large difference between the specific gravity of apples (0.8) and concentrated osmotic solutions. The fruits floated in the osmotic solution, only about 50% submerged. Forcing the fruits into the solution would have resulted in packing and thus a reduction in circulating the concentrated viscous solution between them. Farkas and Lazar (1969) suggested that a way to obtain good circulation and even contact between osmotic solution and fruits might be to convey the apple slices through syrup which was dispersed through sprays over a moving bed. They also found that a pilot plant test using osmotic dehydrofrozen apples resulted in 25% to 50% more cost

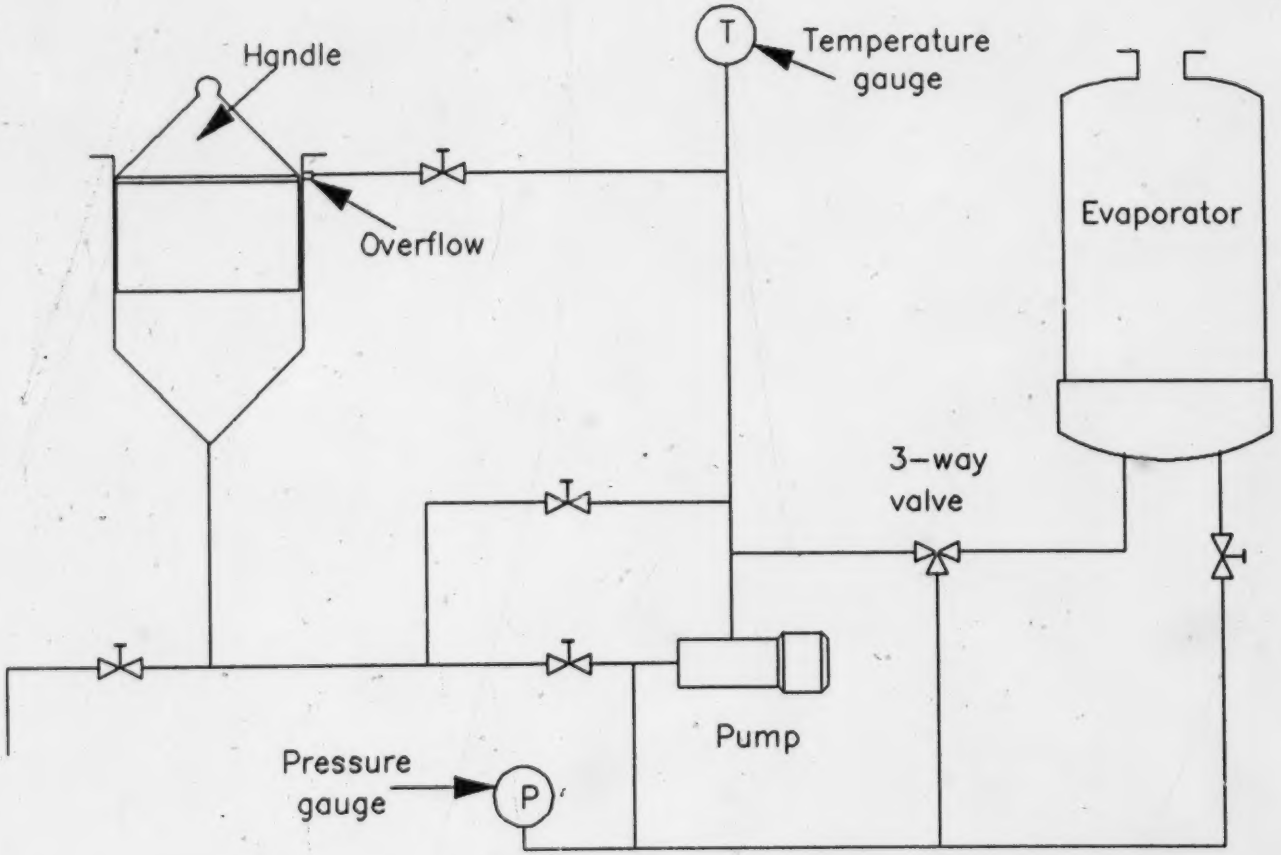

Fig. 2.4. Diagram of Pilot Plant Test (Farkas and Lazar, 1969)

than conventional dehydrofrozen fruits. However, elimination of sulfur dioxide and increased product quality such as sweetness, flavor and color may compensate for the higher cost.

Le Maguer and Biswal (1984) proposed a dehydrocooling process as an intermediate step in the freezing of vegetables and other food products. Fig. 2.5 shows a systematic scheme for an immersion freezing process using dehydrocooling as a preliminary step. Food products such as vegetables pass through the dehydrocooling unit counter-current to the aqueous coolant. The aqueous coolant will be reconcentrated. The partially dehydrated and cooled product will go to an immersion freezing unit.

More recently, a pilot scale batch system for osmotic dehydration of carrot cubes was studied by Guenneugues (1986). The system consisted of a glass fixed-bed container(Fig. 2.6). A metal screen was placed on the top of the carrot cube layer in order to prevent floating. The osmotic solution was circulated through the samples with a flow rate of 9 l/min by a volumetric pump.

2.4.2 Continuous Extraction Process

Although, the batch operation system has been widely used in the food industry for many extraction processes, counter-current leaching processes can most efficiently minimize solvent use as well as solute and solvent recovery costs (Schwartzberg, 1980). Spaninks (1979) also emphasized that the phases are generally contacted in an overall counter-current fashion in order to make efficient use of the solvent.

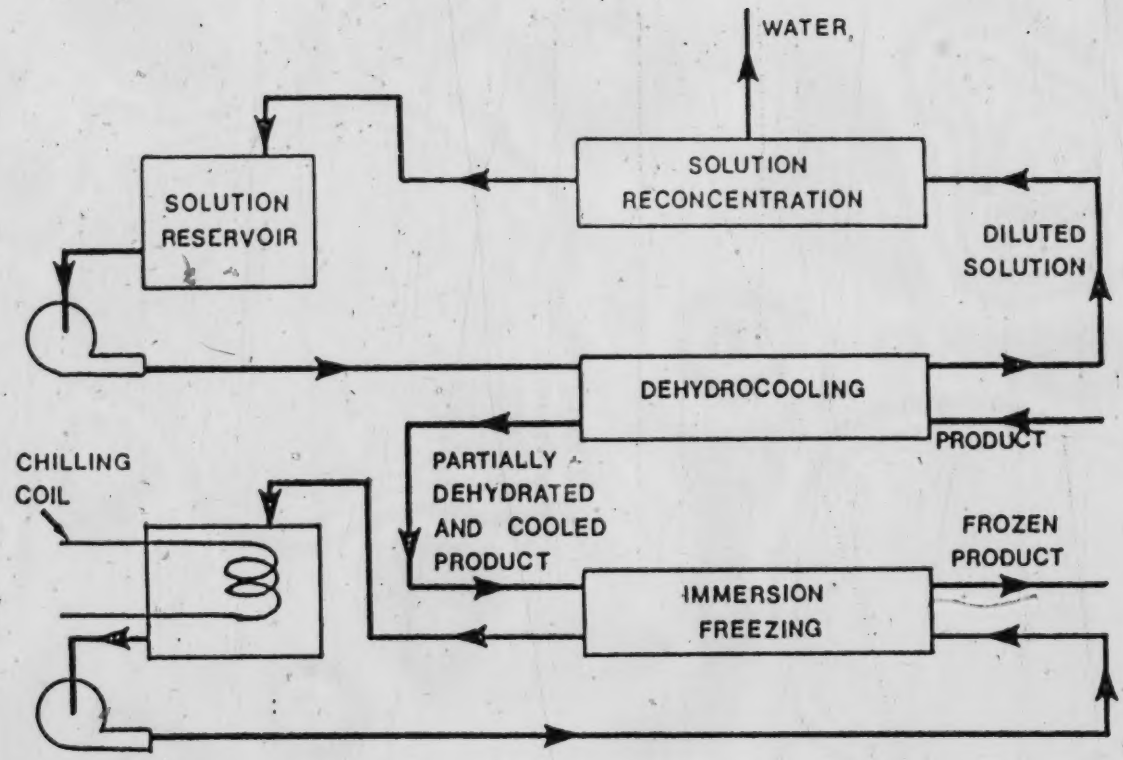

Fig. 2.5 Dehydrocooling as a Preliminary Step in Immersion Freezing

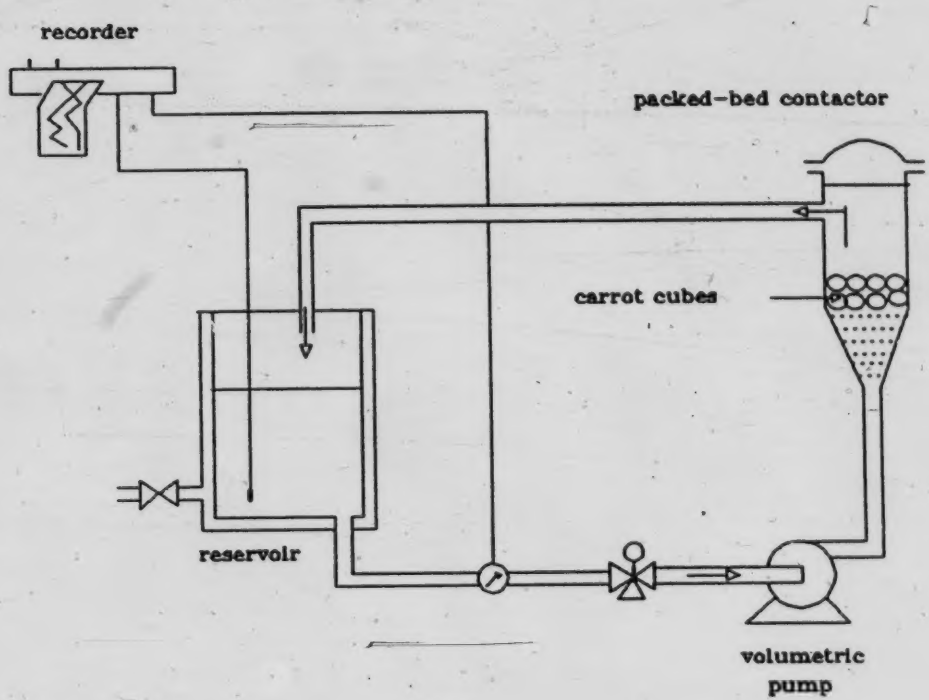

Fig. 2.6 Batch System for Osmotic Dehydration

Schwarzberg (1980) gave a detailed description of leaching apparatus. The majority of these extractors consist of a counter-current cascade of discrete stages in which actual contact takes place (Spaninks, 1979). It is not necessary to have a counter-current flow between solid and liquid phases within each stage. In practice, cross-current stages in belt-type extractors are widely used, while pure counter-current flows are found in the screw types, or diffusion batteries of extractions.

Because of mechanical problems involved in processing large quantities of different solid materials, a variety of extractors of different characteristics and purposes are currently in use.

Little work has been done on the continuous process for osmotic treatment. Based on an analysis of characteristics of extraction processes, it seems that a percolation type of extractor is a potential candidate. In a percolation extractor the solids are transported on a perforated support as a compact bed. The liquid flow is distributed over the bed, percolates downwards by gravity, and leaves the bed dripping through the perforations in the structure supporting the bed of solids (e.g. a perforate bed). The relatively high solid phase hold up makes this extractor attractive for large scale extraction such as extracting oil from oil seeds and sugar from sugar cane.

The operation principle of these extraction systems is shown in Fig. 2.7. According to Spaninks (1979), the description of the working diagram could be as follows: The solvent is distributed over a section of the extractor by spargers and the liquid percolates through the bed of solids by gravity, and after dripping through the perforated support,

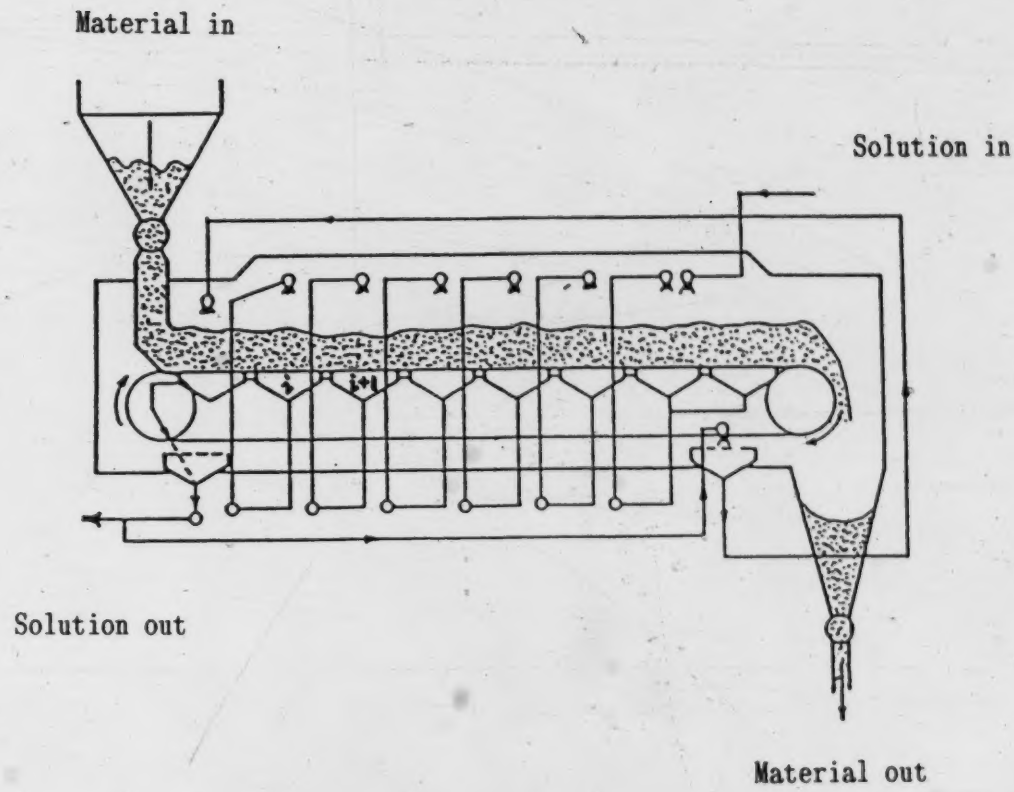

Fig. 2.7 Continuous Counter-current Belt System
(Spaninks, 1979)

it is collected in reservoirs or pans. The net liquid flow from inlet to outlet is accomplished by pumping the extract in section i to the sparger in section i+1. In other cases, the extract from pan i is recirculated in section i while the net liquid flow is obtained by overflow of the collection pans as indicated in Fig. 2.7. Spanink (1979) developed the model for this type of extractor using a NTU (number of transfer unit) approach.

Another possibility is a screw extraction unit. By carefully designing the incline of the screw, the material may remain intact while diffusion takes place.

2.5 Existing Models

When a solid material is placed in a solute-containing environment, mass transport phenomena will take place. As noted, examples of the diffusive transfer of solute from a solid to a surrounding solvent or vice-versa in the food industry are desalting pickles, extracting oil and sugar, decaffeinating coffee, etc.

Molecular diffusion in biological tissue is a very slow process. The rate of mass transfer can be approximately predicted by appropriate solutions of the simplified unsteady state second Fickian equation with an apparent effective diffusivity in the case of a single diffusing component without shrinkage.

According to Crank (1975), the fundamental equation is expressed as:

$$\frac{\partial \bar{C}_i}{\partial \theta} = \frac{\partial}{\partial Z}\left[D_i \frac{\partial \bar{C}_i}{\partial Z} \right] \qquad [2.1]$$

Where $\bar{C}_i$ is the average concentration of component i; θ is time; Z is distance and D_i is the diffisivity.

The transfer is assumed to be unidirectional and effects of other components on the diffusion of the solute are negligible. For idealized geometries i.e. spheres, infinite cylinders, infinite slabs, and semi-infinite mediums, analytical solutions of equation [2.1] are available (Crank, 1975).

For diffusion in porous media, the effective diffusivity is lower than the diffusion coefficient in other situations. We can thus relate diffusivity of this specie in solution to the apparent diffusivity in a porous solid by a correction factor that contains the void fraction and the tortuosity.

Many authors have attempted to apply an unsteady-state Fickian diffusion equation to an extraction process such as desalting and sugar extraction. Drusas and Vagenas (1988) investigated diffusivity of sodium chloride in green olives using the unsteady-state diffusion equation under defined initial and boundary conditions. This technique was applied to the diffusion of salt in cucumbers immersed in an agitated solution of limited volume as well (Pflug *et al.*, 1967). Soddu and Gioia (1979) tried to model sugar extraction process from a beet immersed in water using the unsteady-state second-order Fickian equation. In this analysis, an effective diffusion coefficient was corrected for the void fraction and the tortuosity. All these applications are based on a large number of assumptions as mentioned

previously.

Hawkes and Flink (1978) studied the kinetics of mass transport in the osmotic process. They found that the unsteady-state Fickian diffusion model may apply if external solution concentrations remain constant, and resistance at the surface is negligible compared to internal diffusion resistance. It is acceptable for the first condition if the ratio between the osmotic solution and the amount of sample material is relatively large.

However, in most cases, the external resistance is not negligible, especially at higher concentrations of osmotic solution. Hawkes and Flink (1978) expressed their results as the percent total solids change per unit initial total solids basis (i.e. normalized solid content, NSC)

$$(NSC) = K\ (t)^{1/2} \qquad [2.2]$$

where K is defined as the mass transfer coefficient which is determined from the slope of the NSC versus $(t)^{1/2}$ curves.

Conway et al (1983) proposed a mathematical model for mass transfer phenomena in osmotic dehydration in a sucrose solution using the second-order Fickian equation assuming a simple diffusion of water occurring upon osmosis. The apparent diffusion coefficient D was evaluated empirically and multilinear analysis revealed that D depended on temperature in addition to the combined effect of both parameters

Hawkes and Flink (1978) tried to estimate the diffusion coefficients assuming unsteady-state diffusion in a semi-infinite

medium. However, the unsteady-state Fickian equation is not appropriate to simulate an osmotic process, since there is more than one flow taking place. The simultaneous water loss and solids gain is a very important characteristic of this process. As Lerici et al (1985) pointed out it is important to take into account not only the weight reduction and the water loss but also the solids gain. Furthermore, shrinkage also occurs during such a process.

Spaninks (1979) applied the number of transfer unit (NTU) approach or mass transfer coefficient approach for the design of a solid-liquid extractor and he proposed models for many different types of extraction systems such as batteries, multi-cell, deep bed, belt type etc. The mass transfer coefficients used in such analyses can be obtained from asymptotic approximations derived for diffusion controlled mass transfer. His analysis used iterative corrections to estimate inlet extract feed concentration versus time profiles. This was done to generate extract and solid concentration versus time profiles.

A number of factors were considered, such as liquid recirculation, delayed drainage, and liquid reapplication. Apparently this analysis does not take into account such contacting imperfections as imcomplete bed coverage by the fluid due to excessively rapid drainage on liquid channeling in uncovered bed regions (Schwartzberg, 1980). The rate and extent of leaching depends on the mass transfer Fourier number Dt/a^2 , where D is the diffusivity of the solute in the solid, t is the contact time and a is a characteristic dimension of the solid (Schwartzberg, 1980).

Generally, for this kind of approach, the design of mass transfer

processes starts from specified or assumed concentrations in inlet and outlet streams and flow rates. The mass flux that occurs in solid-liquid extractors is often proportional to the overall driving force for mass transfer. In such cases, the NTU concept, in which the mass transfer resistance is lumped at the solid-liquid interface, is a convenient basis for a design procedure.

Most of the diffusional mass transfer studies on food systems reported in the literature deal with either binary processes (Fick's law description) or assume independence of the movement of each species in multicomponent systems (Pflug *et al.*, 1967; Menting *et al.*, 1970). According to Bailey's (1975) a concentration independent individual diffusivity based on weight in a multicomponent system overestimates the amount diffused because of the exclusion of the interaction between the components. The only literature to date in food systems where interaction between components has been taken into account is that of Chandrasekaran and King (1972). Their study of multicomponent diffusion in a ternary system, sucrose, ethanol and water, was based on the thermodynamics of irreversible processes (Miller, 1960; Wisniewski, *et al.*, 1976).

The mass transport of material through membranes near equilibrium can be described by systems of linear equation known as Onsager phenomenological equations (Toupin., 1986).

The flow of slow, irreversible processes near equilibrium can be assumed to be directly proportional to their driving forces (Katchalsky *et al.*, 1976).

$$J_i = \Sigma_j L_{ij} \Delta\mu_j \qquad i,j = 1,2,\ldots\ldots,n \qquad [2.3]$$

Flux is proportional to the driving force $\Delta\mu_j$ (difference in chemical potential) by a phenomenological coefficient L_{ij}. The driving force is expressed as:

$$\Delta\mu_j = R\ T\ \Delta\ln a_j + V_j\Delta P + Z_j F\ \Delta\phi \qquad [2.4]$$

where R is the universal gas constant, T is the absolute temperature of the system, $\Delta\ln a_j$ is the gradient of molecular potential, ΔP the hydrostatic pressure difference between osmotic solutions on both sides of the membrane and $\Delta\phi$ the electrical potential difference, V_j and Z_j are the partial molar volume and the electrical charge of species j; F is the Faraday constant.

The main advantage of Eq. [2.3] is that it takes in to account non-ideal solutions containing ions by the use of the chemical potential as the driving force (Eq. 2.4).

In the linear range of equation 2.3, these coefficients are symmetrical ($L_{ij} = L_{ji}$). Moreover, based on theoretical considerations (Wisniewski *et al.*, 1976), they are constrained within a certain range, that is:

$$L_{ii} > 0 \qquad [2.5]$$

and

$$|L_{ij}| \leq \sqrt{L_{ii}\ L_{jj}} \qquad [2.6]$$

which means that straight-coefficients must always be larger than zero, and the cross-coefficients can be either positive or negative when transport of species i and species j are in an opposite direction.

In the non-linear range, applying Tayor's series expansion, the fundamental form of the phenomenological relations Eq. [2.3] becomes:

$$J_i = \Sigma_j K_{ij} \Delta\mu_j/T + 0.5 \Sigma_{jk} K_{jk}(\Delta\mu_j/T \Delta\mu_k/T) +$$

$$+0.5 \Sigma_j K_{ij} (\Delta\mu_j/T)^2 \qquad [2.7]$$

$$i,j,k = 1,2,.....,n$$

where again symmetry relations apply (Sauer, 1973).

Based on equation 2.7, Guennegues (1986) approached the mass transfer in multicomponent systems occurring in plant tissue upon osmosis, taking into account the fluxes of the different components of the system and the interactions between the different fluxes.

The component fluxes were described using equations such as 2.8, 2.9 below:

$$J_i = K_{ww} \frac{\Delta\mu_w}{T} + K_{ws} \frac{\Delta\mu_s}{T} + K'_{ww} (\frac{\Delta\mu_s}{T})^2 + K'_{ws} (\frac{\Delta\mu_w}{T})^2 + K''_{ws} \frac{\Delta\mu_s}{T} \frac{\Delta\mu_w}{T} \qquad [2.8]$$

$$J_s = K_{ss}\frac{\Delta\mu_s}{T} + K_{sw}\frac{\Delta\mu_w}{T} + K'_{ss}\left(\frac{\Delta\mu_s}{T}\right)^2 + K'_{sw}\left(\frac{\Delta\mu_w}{T}\right)^2 + K''_{sw}\frac{\Delta\mu_s}{T}\frac{\Delta\mu_w}{T} \qquad [2.9]$$

where J_w an J_s represent the fluxes of water and salt, K_{ij} and K''_{ij} are mass transfer coefficients and $\Delta\mu_i$ is the chemical potential gradient for mass transfer.

Numerous studies have been done on the partial removal of water from solid materials by osmosis. The quantity and the rate of water removal depend on several parameters. In general, it has been mentioned that the water loss in osmosed products is increased by increasing the solute concentration, contact time, temperature and solution/food ratio. However, most studies were restricted to an experimental batch condition which is difficult to scale up for commercial production. Continuous process is recognized as the most efficient process. Studying osmotic behavior and modelling the mass transport phenomenon in plant materials on a continuous process have never been conducted. There is a lack of reliable information and accurate data to demonstrate the feasibility of applying osmotic processes to commercial operation. On the basis of the previous review, we set to build a pilot plant contactor to obtain raw data for modelling purpose. The phenomenological approach of Guenneugues (1986) extended to 3 components will be used to model the fluxes and a mathematical model will be developed for prediction of mass change along the contactor.

3 THEORY AND MODEL DEVELOPMENT

3.1 Modeling a Single Carrot Cube

3.1.1 Important Components and Mathematical Treatment of Carrot Tissue

Biological tissues are mostly porous or cellular substances in which a liquid and/or a gas are immobilized in a solid matrix. Carrots are cellular in structure with an insoluble matrix. The average composition of carrot is presented in Appendix 1. One may represent it as a liquid phase which includes water (W_w), sugar (W_{su}), salt (W_{sc}), soluble solids (W_{ss}, non-sugar and non-salt) and insoluble matrix (insoluble solids, W_{in}).

Modeling a five component system is difficult because of the large number of variables involved. Therefore, a simplification of the carrot tissue is desirable for modeling purpose. The average composition of the carrot tissue was used. Since insoluble solids provide a matrix which does not contribute to the mass transport or the chemical potential, the effect of the insoluble solids can be eliminated by reevaluating the weight fraction of other components.

That is:

$$W_{su}^{cor} = \frac{W_{su}}{1 - W_{in}} \qquad [3.1]$$

and

$$W_{sc}^{cor} = \frac{W_{sc}}{1 - W_{in}} \qquad [3.2]$$

and

$$W_{ss}^{cor} = \frac{W_{ss}}{1 - W_{in}} \qquad [3.3]$$

and

$$W_{w}^{cor} = 1 - W_{su}^{cor} - W_{sc}^{cor} - W_{ss}^{cor} \qquad [3.4]$$

where W_{su}, W_{sc}, W_{in}, W_{w} and W_{ss} are the weight fraction of sugar, sodium chloride, insoluble solids, water and soluble solids in the original carrot tissue, W_{su}^{cor}, W_{sc}^{cor}, W_{ss}^{cor} and W_{w}^{cor} are the corrected weight fractions of sugar, sodium chloride, soluble solids and water.

With a simple system of a single carrot cube immersed in an osmotic medium, mass transfer occurs across the interface. In general, the total resistance to the transport of any component is the sum of the surface resistance due to convective flow, the internal resistance due to diffusional flow and resistance from the complex membrane and the cell wall. All these resistances may be lumped into a single resistance equivalent to a pseudo-membrane. Therefore, for modeling convenience, this system is considered as two individual compartments, a carrot cube and a surrounding osmotic medium which are separated by a pseudo-membrane as shown in Fig. 3.1. Each of the compartment is assumed to be continuous with a multi-component liquid phase consisting of permeable and impermeable species.

According to Sauer (1973), the internal change of entropy of such a system due to irreversible processes in the membrane, $\frac{dS_i}{d\theta}$ is given by

$$\frac{dS_i}{d\theta} = J_u^{(2)} \Delta \frac{1}{T} + \sum_{k=0}^{n} J_k^{(1)} \Delta \frac{\mu_i}{T}$$

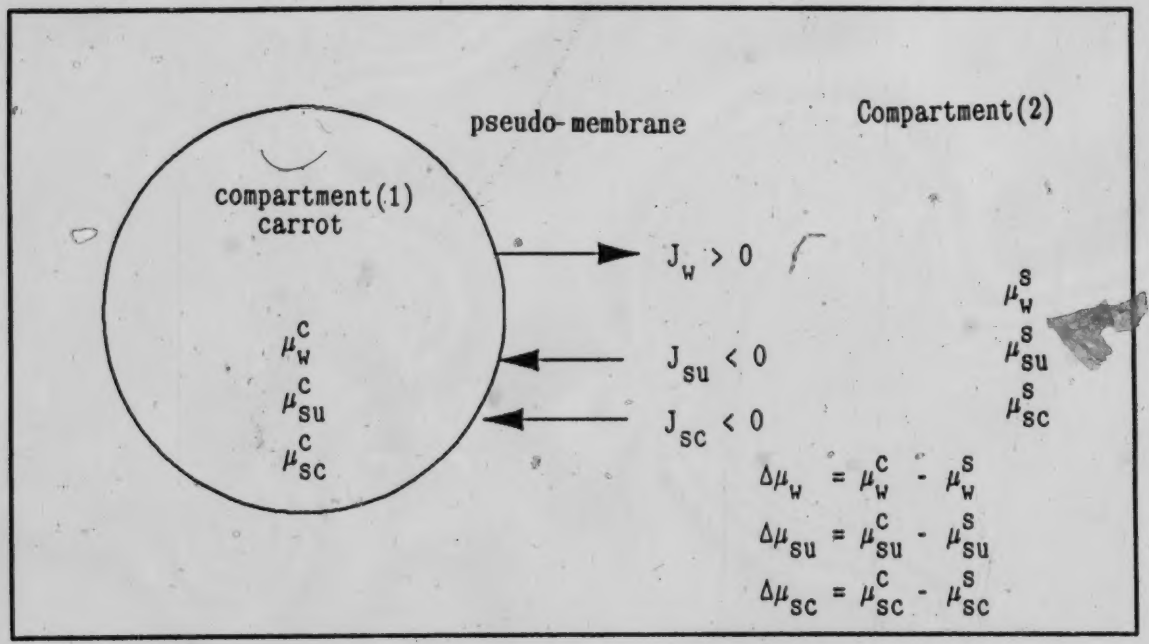

Fig. 3.1 Schematic Representation of the Model for Mass Transfer Study

$$k = 1, 2, \ldots\ldots n \qquad [3.5]$$

where $J_u^{(2)}$ refers to energy flow of compartment(2), Δ is defined as the difference between quantities in compartment(2) and compartment(1). For the detailed derivation of Eq. [3.5] refer to Sauer (1973).

The process is considered to move from a nonequilibrium state towards an equilibrium state with respect to the distribution of components in each compartment. As shown in Fig. 3.1, this nonequilibruium state will be characterized by the flow of component i on the two sides of the pseudo-membrane.

3.1.2 Representation of Flux in a Single Carrot Cube

For a carrot cube with positive x-direction away from the centre, the flux of component i relative to the moving interface may be written as:

$$J_i = -\frac{1}{A}\left[\frac{dM_i}{dt}\right] \qquad [3.6]$$

where A is a surface area of a carrot cube, M_i is the mass of component i at time t.

The mass transfer surface per unit mass is difficult to evaluate due to the irregular shape of the cubes and the overlapping of carrot cubes in the bed. A simplification was made whereby the carrot cubes were assumed all of regular shape and the solution filled all the void

in the bed of carrots. Therefore, the mass transfer surface per unit mass simply becomes:

$$A_{cube} = 6\ a^2 \qquad [3.7]$$

$$m_{cube} = a^3\ \rho_c \qquad [3.8]$$

So:

$$\frac{A_{cube}}{m_{cube}} = \frac{6}{a\rho_c} \qquad [3.9]$$

Where A_{cube} is a surface area of a carrot cube; m_{cube} is the mass of a cube; a and ρ_c are the side length of a cube and the carrot density.

3.1.3 Thermodynamic Representation of Flux

From Eq. [2.7]

$$J_i = \Sigma_j\ K_{ij}\ \Delta\mu_j/T + 0.5\ \Sigma_{jk}\ K_{jk}(\ \Delta\mu_j/T\ \Delta\mu_k/T\ )$$

$$+0.5\ \Sigma_j\ K_{ij}\ (\Delta\mu_j/T)^2 \qquad [2.7]$$

$$i,j,k = 1,2,\ldots\ldots,n$$

From identification of the important components in the carrot tissue, there are 4 components in compartment(1), that is: water, sugar, salt and soluble solids. There are only 3 components in compartment(2)

(osmotic solution). In order to calculate the driving force ($\Delta\mu_i$) between the compartments, the quaternary system in the liquid phase of carrot tissue can be brought down to a ternary system. Because only sucrose, salt, water are of interest, soluble solids were transformed into an equivalent sodium chloride concentration based on an equivalent osmotic pressure condition. The salt concentration equivalent to the soluble solids is calculated as

$$W_{ss}^{eq} = 0.166 \times W_{ss}^{cor} \qquad [3.10]$$

Then the weight fractions of the other components are:

$$W_{sc}^{eq} = \frac{(W_{ss}^{eq} + W_{sc}^{cor})}{(W_{ss}^{eq} + W_{sc}^{cor} + W_{su}^{cor} + W_{w}^{cor})} \qquad [3.11]$$

and

$$W_{su}^{eq} = \frac{W_{su}^{cor}}{(W_{ss}^{eq} + W_{sc}^{cor} + W_{su}^{cor} + W_{w}^{cor})} \qquad [3.12]$$

and

$$W_{w}^{eq} = 1 - W_{su}^{eq} - W_{sc}^{eq} \qquad [3.13]$$

where W_{ss}^{eq} is the weight fractions of soluble solids equivalent to that of sodium chloride, W_{sc}^{eq}, W_{su}^{eq} and W_{w}^{eq} are the equivalent weight fractions

of sodium chloride, sucrose and water in carrot tissue.

Hence, with this approximation, the system can be analyzed based on a pseudo-ternary basis. The three components are: (1) sucrose, (2) NaCl and (3) water in these two compartments. In the case of osmotic dehydration with a ternary aqueous solution, sucrose/sodium chloride/water, as we analyzed previously, the peudo-membrane separates the internal solution in compartment (1) and external solution in compartment (2). There are three major fluxes simultaneously taking place; the flux of water (J_w), the flux of sucrose (J_{su}) and the flux of sodium chloride (J_{sc}). According to Eq. [2.7], the flux of water can be extanded as follows:

$$J_w = K_{w,w}\frac{\Delta\mu_w}{T} + K_{w,su}\frac{\Delta\mu_{su}}{T} + K_{w,sc}\frac{\Delta\mu_{sc}}{T} + K'_{w,su}\frac{\Delta\mu_{su}}{T}\frac{\Delta\mu_w}{T}$$
$$+ K'_{w,sc}\frac{\Delta\mu_{sc}}{T}\frac{\Delta\mu_w}{T} + K'_{su,sc}\frac{\Delta\mu_{su}}{T}\frac{\Delta\mu_{sc}}{T}$$
$$+ K''_{ww}\left(\frac{\Delta\mu_w}{T}\right)^2 + K''_{w,su}\left(\frac{\Delta\mu_{su}}{T}\right)^2 + K''_{w,sc}\left(\frac{\Delta\mu_{sc}}{T}\right)^2 \qquad [3.14]$$

Similarly, the flux of sucrose (J_{su}) can be expressed as:

$$J_{su} = K_{su,w}\frac{\Delta\mu_w}{T} + K_{su,su}\frac{\Delta\mu_{su}}{T} + K_{su,sc}\frac{\Delta\mu_{sc}}{T} + K'_{su,w}\frac{\Delta\mu_{su}}{T}\frac{\Delta\mu_w}{T}$$
$$+ K'_{sc,w}\frac{\Delta\mu_{sc}}{T}\frac{\Delta\mu_w}{T} + K'_{su,sc}\frac{\Delta\mu_{su}}{T}\frac{\Delta\mu_{sc}}{T}$$
$$+ K''_{su,w}\left(\frac{\Delta\mu_w}{T}\right)^2 + K''_{su,su}\left(\frac{\Delta\mu_{su}}{T}\right)^2 + K''_{su,sc}\left(\frac{\Delta\mu_{sc}}{T}\right)^2 \qquad [3.15]$$

And the flux of sodium chloride (J_{sc}):

$$J_{sc} = K_{sc,w}\frac{\Delta\mu_w}{T} + K_{sc,su}\frac{\Delta\mu_{su}}{T} + K_{sc,sc}\frac{\Delta\mu_{sc}}{T} + K'_{w,su}\frac{\Delta\mu_{su}}{T}\frac{\Delta\mu_w}{T}$$

$$+ K'_{w,sc}\frac{\Delta\mu_{sc}}{T}\frac{\Delta\mu_w}{T} + K'_{su,sc}\frac{\Delta\mu_{su}}{T}\frac{\Delta\mu_{sc}}{T}$$

$$+ K''_{sc,w}(\frac{\Delta\mu_w}{T})^2 + K''_{sc,su}(\frac{\Delta\mu_{su}}{T})^2 + K''_{sc,sc}(\frac{\Delta\mu_{sc}}{T})^2 \qquad [3.16]$$

where K_{ij}, K'_{ij} and K''_{ij} are phenomenological coefficients. Eq. [3.14], Eq. [3.15] and Eq. [3.16] will be used to describe the mass transfer fluxes and thermodynamic forces in the osmotic dehydration of carrots.

3.2 Modeling a Contactor

3.2.1 Assumption

The first approximation is that the osmotic solution has a constant concentration during the process, which means that the chemical potential on the solution side (μ_i^s) does not change, only the chemical potential in the carrot tissue changes during the process.

Since

$$\Delta\mu_i = \mu_i^c - \mu_i^s \qquad [3.17]$$

If μ_i^s remains constant, the difference in chemical potential ($\Delta\mu_i$) is only a function of the change in carrot compositions resulting from different contact time. The second assumption is that there is no

concentration gradient throughout the thickness of the bed of carrot cubes at a given position on the belt (the average thickness of bed of carrots is about 2cm). Therefore, the materials on the belt in Fig. 3.2(a) can be represented as one dimensional (see Fig. 3.2(b)). A computer simulation program was developed to determine the properties of the materials along the contactor as a function of time or distance (Fig. 3.3).

3.2.2 Mathematical Models

As mentioned, the rate of water, sucrose and sodium chloride mass change in carrot cubes as a function of time may be expressed as:
Recall Eq. [3.6]

$$J_i = - \frac{1}{A} \left[\frac{dM_i}{dt} \right]$$

Thus

$$\frac{dM_i}{dt} = - A J_i$$

So

$$\frac{dM_w}{dt} = - A J_w \qquad [3.18]$$

and

$$\frac{dM_{su}}{dt} = - A J_{su} \qquad [3.19]$$

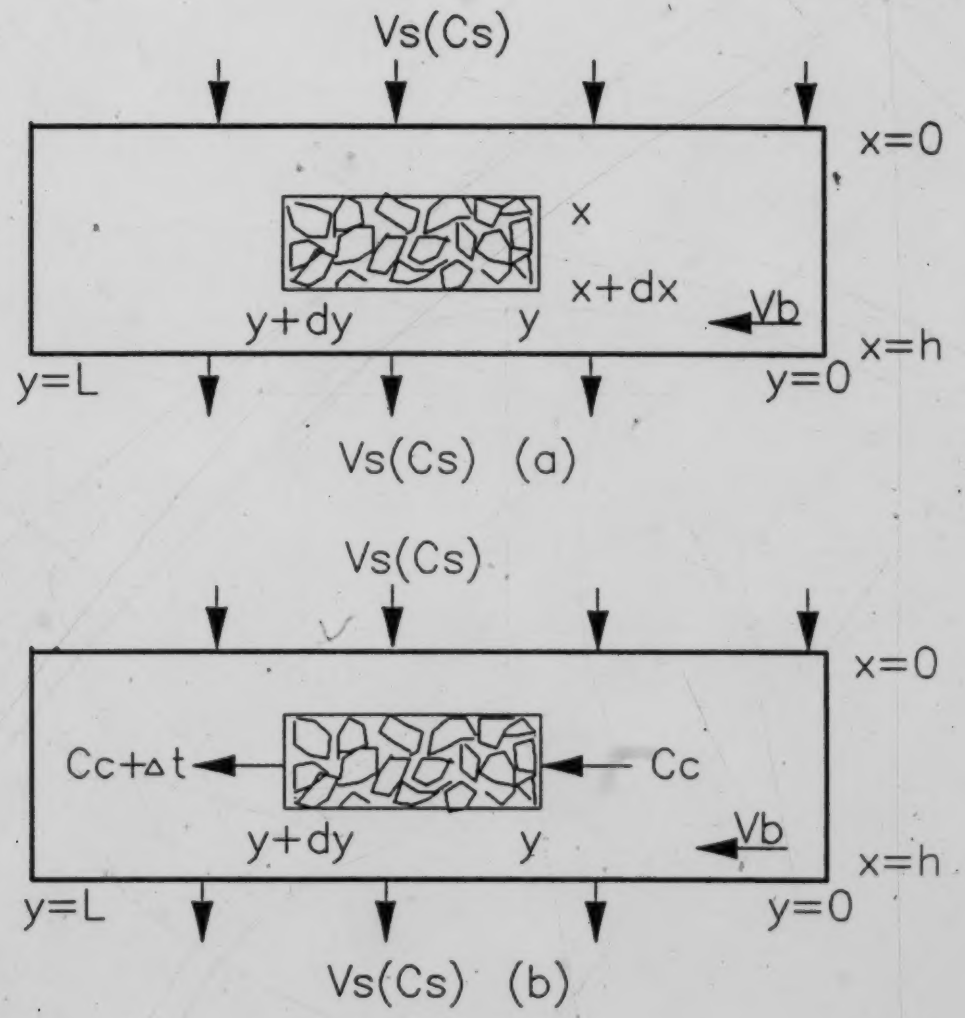

Fig. 3.2 Schematic Representation of Contactor

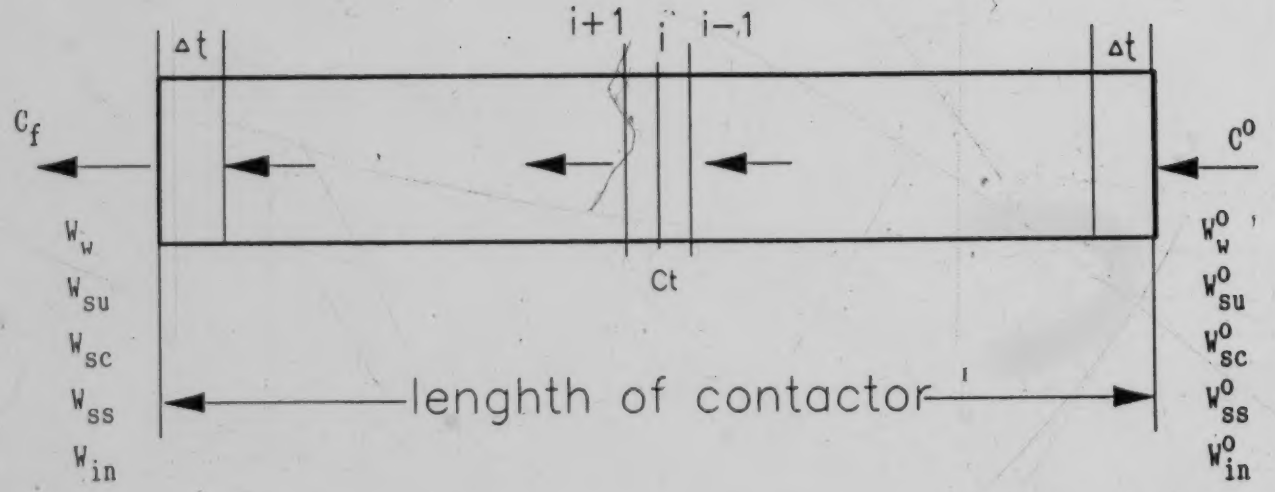

Fig. 3.3 Continuous Cross-current Coupled with Counter Current Contactor

and

$$\frac{dM_{sc}}{dt} = - A J_{sc} \qquad [3.20]$$

The rate of mass change of the carrot cubes is:

$$\frac{dM}{dt} = - A (J_w + J_{su} + J_{sc}) \qquad [3.21]$$

where J_w, J_{su} and J_{sc} are the fluxes of water, sucrose and sodium chloride (kg/m^2s), A is the unit surface area of the carrot cubes.

Because:

$$M_w = M W_w \qquad [3.22]$$

The derivative of M_w is,

$$\frac{dM_w}{dt} = W_w \frac{dM}{dt} + M \frac{dW_w}{dt} \qquad [3.23]$$

So:

$$\frac{dW_w}{dt} = \frac{1}{M} \left[\frac{dW_w}{dt} - W_w \frac{dM}{dt} \right] \qquad [3.24]$$

Combine Eq. [3.6], Eq.[3.21] and Eq. [3.24]

Then,

$$\frac{dW_w}{dt} = \frac{A}{M}\left[(W_w - 1)\, J_w + W_w\, J_{su} + W_w\, J_{sc} \right] \qquad [3.25]$$

where W_w is the weight fraction of water at time t.

Similarly:

$$\frac{dW_{su}}{dt} = \frac{A}{M}\left[W_{su}\, J_w + (W_{su} - 1)\, J_{su} + W_{su}\, J_{sc} \right] \qquad [3.26]$$

and

$$\frac{dW_{sc}}{dt} = \frac{A}{M}\left[W_{sc}\, J_w + W_{sc}\, J_{su} + (W_{sc} - 1)\, J_{sc} \right] \qquad [3.27]$$

Where W_{su} and W_{sc} are weight fraction of sucrose and sodium chloride at time t.

Remember Eq. [3.9] for a single cube:

$$\frac{A_{cube}}{m_{cube}} = \frac{6}{a\rho_c}$$

For an unit mass of carrot cubes, we assume here that the cubes are in total contact with the solution without loss of contact area:

$$M = V\, \rho_b \qquad [3.28]$$

where ρ_b is the bulk density of an unit mass, V is the volume of the unit mass.

The number of cubes in the unit mass:

$$n = \frac{M}{m_{cube}} = \frac{M}{\rho_c a^3} \qquad [3.29]$$

The total surface area of n cubes:

$$A = A_{cube}\, n$$

$$= (6a^2)\, \frac{M}{\rho_c a^3}$$

$$= \frac{6M}{a\rho_c} \qquad [3.30]$$

Thus: $$\frac{A}{M} = \frac{6}{a\rho_c} \qquad [3.31]$$

where ρ_c is the density of carrot cubes, a is the side length of carrot cube and M is the mass of carrot cubes (function of time).

Introducing M_o into Eq. [3.6], it becomes:

$$J_i = - \frac{M_o}{A} \left[\frac{d(M_i/M_o)}{dt} \right] \qquad [3.32]$$

where M_o is the mass of carrots at time zero.

Combining Eq. [3.31] and Eq. [3.32]

$$J_i = - \frac{a\rho_c}{6\, \frac{M}{M_o}} \left[\frac{d(\frac{Mi}{Mo})}{dt} \right] \qquad [3.33]$$

The variation of ρ_c due to the shrinkage was taken into consideration in the simulation, for five components system in the carrots, the density ρ_c, can be written as:

$$\frac{1}{\rho_c} = \frac{W_w}{\rho_w} + \frac{W_{su}}{\rho_{su}} + \frac{W_{sc}}{\rho_{sc}} + \frac{W_{in}}{\rho_{in}} + \frac{W_{ss}}{\rho_{ss}} \qquad [3.34]$$

where ρ_w is the density of water at 25°C, ρ_w = 1000 kg/m^3; ρ_{su} is density of sucrose, ρ_{su} = 1580 kg/m^3; ρ_{sc} is the density of sodium chloride; ρ_{sc} = 2165 kg/m^3; ρ_{in} is the density of insoluble solids. Because the insoluble solids matrix in plant materials, are mainly cellulose and semicellulose , ρ_{in} is taken as an average around 1500 kg/m^3; ρ_{ss} is the density of soluble solids which is approximately around 1800 kg/m^3 (CRC, 1975). Because of the shrinkage, the change in the volume of a carrot cube is given by:

$$\frac{dV_c}{dt} = - A (J_w \nabla_w + J_{su} \nabla_{su} + J_{sc} \nabla_{sc}) \qquad [3.35]$$

$$\frac{da^3}{dt} = - 6a^2 (J_w \nabla_w + J_{su} \nabla_{su} + J_{sc} \nabla_{sc}) \qquad [3.36]$$

Thus, the change of a side of carrot cube:

$$\frac{da}{dt} = - 2 (J_w \nabla_w + J_{su} \nabla_{su} + J_{sc} \nabla_{sc}) \qquad [3.37]$$

where V_w, V_{su} and V_{sc} are partial specific volumes of water, sucrose and sodium chloride on average. Eq. [3.21], to Eq.[3.37] are models used for the computer simulation along the contactor.

3.3 Difference in Chemical Potential as Driving Forces

Phenomenological Eq. [2.3] states that flux is proportional to the sum of driving forces presented in the system. In order to predict the flux of the species i through Eq. [2.3], it is necessary to follow the change of the component chemical potentials. In the equation [2.3], $\Delta\mu_i$ is the difference in chemical potential of species i across the pseudo-membrane; i.e:

$$\Delta\mu_i = \mu_i^{in} - \mu_i^{out} \qquad [3.38]$$

where μ_i^{in} is the chemical potential of species i inside the cellular volume and μ_i^{out} is chemical potential of the species i in the extracellular volume.

Since we have assumed that the pseudo-membrane separates the solution inside the carrot cube from the osmotic solution outside, in this case sucrose/scdium chloride/water system, the differences in chemical potential can be expressed as follows:

$$\Delta\mu_w = \mu_w^c - \mu_w^s \qquad [3.39]$$

and

$$\Delta\mu_{su} = \mu_{su}^c - \mu_{su}^s \qquad [3.40]$$

and

$$\Delta\mu_{sc} = \mu^{c}_{sc} - \mu^{s}_{sc} \qquad [3.41]$$

where $\Delta\mu_{w}$, $\Delta\mu_{su}$, $\Delta\mu_{sc}$ are the differences in chemical potentials in water, sucrose and sodium chloride between the liquid phase of carrot cubes and the osmotic solutions, respectively. μ^{c}_{w} , μ^{c}_{su} and μ^{c}_{sc} are the chemical potential of water, sucrose and sodium chloride in the liquid phase of the carrot cube respect to a reference state calculated from the knowledge of the average concentrations. And μ^{s}_{w}, μ^{s}_{su} and μ^{s}_{sc} are the chemical potentials of water, sucrose and sodium chloride in the osmotic solutions with respect to a same reference state as the carrot cubes.

3.3.1 Chemical Potentials of Water, Sucrose and Sodium Chloride

Most thermodynamic treatment considers the sucrose/sodium chloride/water system as a mixed solvent system. The electrolytes are assumed to be completely disassociated. The chemical potential of water can be calculated as:

$$\mu_{w} = R\,T\,\ln(\gamma_{w}\,x_{w}) \qquad [3.42]$$

where γ_{w} is the activity coefficient of water and x_{w} is the mole fraction of water.

$$x_w = \frac{\left[\frac{W_w}{MW}\right]}{\left[\frac{W_w}{MW} + \frac{W_{su}}{MSU} + 2\frac{W_{sc}}{MSC}\right]} \qquad [3.43]$$

where W_w, W_{su} and W_{sc} are the weight fractions of water, sucrose and sodium chloride, MW, MSU and MSC are the molecular weight of water, sucrose and salt, respectively.

The chemical potential of sucrose can be expressed as:

$$\mu_{su} = R\ T\ \ln(\gamma_{su}\ x_{su}) \qquad [3.44]$$

where γ_{su} and x_{su} are the activity coefficient of sucrose and the mole fraction of sucrose.

$$x_{su} = \frac{\left[\frac{W_{su}}{MSU}\right]}{\left[\frac{W_w}{MW} + \frac{W_{su}}{MSU} + 2\frac{W_{sc}}{MSC}\right]} \qquad [3.45]$$

The chemical potential of the ions can be written as:

$$\mu_{sc} = R\ T\ \ln(\gamma_{sc}\ m_{sc})^2 = 2\ R\ T\ \ln(\gamma_{sc}\ m_{sc}) \qquad [3.46]$$

where γ_{sc} is the mean activity coefficient of the ions and m_{sc} is molality of sodium chloride

$$m_{sc} = \frac{\frac{Wsc}{MSC}}{\frac{W_w}{1000}} \qquad [3.47]$$

The activity coefficient of each component in the ternary mixture are calculated using an extended UNIQUAC equation (Christiensen *et al.*, 1983) through a subroutine developed by Lee (1987). This equation includes a new model for strong completely dissociated electrolytes in pure and mixed solvents.

4 EXPERIMENTAL

4.1 Design of a Contactor to Provide a Continuous Operation

4.1.1 Basic Considerations

To establish the proper conditions for a continuous osmotic process requires a substantial research effort if it is eventually to become a commercial reality. Pilot-scale osmotic equipment should be capable of being scaled up while remaining efficient for osmosis purposes. The basic considerations for designing a continuous osmotic unit are:

a) Properties of the materials to be processed:
   1) physical properties of raw materials (e.g. composition, bulk density, size, shape, etc.)
   2) desired final product quality (appearance, flavour, texture and aroma)

b). Equipment specifications:
   1) continuous counter-current or cross-current coupled with counter-current
   2) processing capacity
   3) separation method
   4) loading method
   5) process control (manual, automatic)
   6) materials (purity, contamination and sanitation)
   7) process economics (capital and operation cost)

It is generally considered in the food industry that the properties

of processed materials have a strong influence on the design of process equipment. As mentioned in Chapter 2, different plant materials exhibit very different behavior upon osmosis.

Based on these requirements and characteristics of the osmotic process as well as the analysis of some of the processing equipment used in extraction, an attempt was made to design a perforated belt osmotic system, which is referred to throughout this paper as the contactor.

4.1.2 Contactor

Fig 4.1 shows the diagram of the contactor. It can be seen that this unit consists of a perforated belt maintained with four pulleys, one of which is connected to a motor drive and gear box and an adjustable belt tension device. The system is supported by a frame on which three collecting pans were arranged in such a manner that the external flow of osmotic solutions from one to the next is conducted by overflow, and the overall flow is counter-current to the belt movement.

Three parallel sprays with their own attachments distribute the solution evenly. The width of the spraying attachments is about 1 cm wider than the width of the belt. These sprays divide the belt (1 m x 0.12 m) into three sections. There is a collecting pan under each section.

As indicated on the diagram, the internal circulation of osmotic solution is obtained by pumping the osmotic solution from the bottom of each collecting pan and spraying it on top of the belt. The internal flow is measured in its own section by a flow meter. The movement of

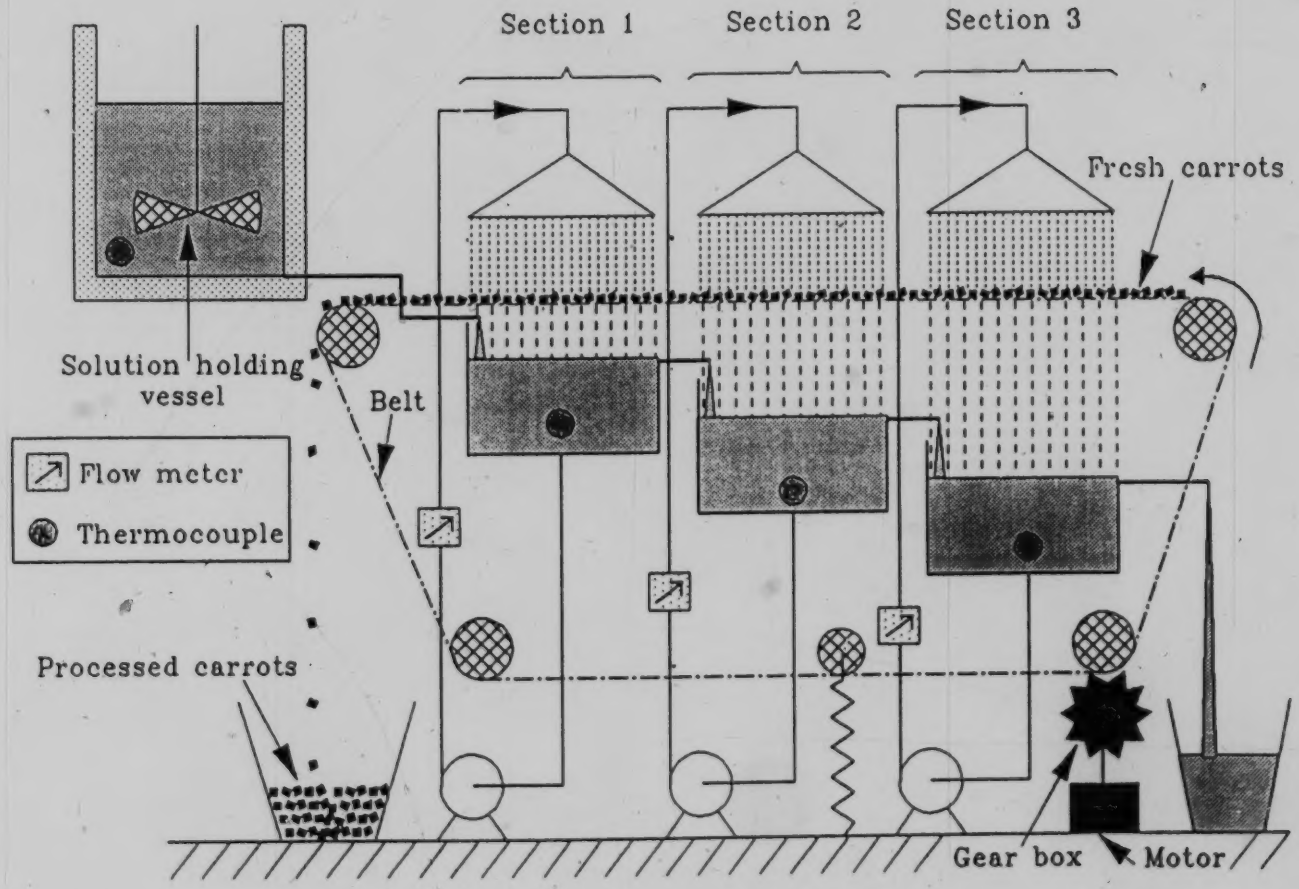

Fig. 4.1 The Diagram of the Contactor

the belt is controlled by a gear box with four speed levels powered by a motor. A double jacketed vessel is used to control the temperature of the osmotic solution with hot water. Four thermocouples are attached to the system, one in the jacketed vessel and one in each collecting pan to measure their respective temperatures. These thermocouples and flow meters are connected to a data logger (Hanzon, DDL-4020) and results are printed out by a printer (Okidata Microline 182) at specified intervals.

The belt material is a very important component in this unit. It should be resistant to abrasion, gasoline, acids or other oxidizing substances and also high temperature. It is also important that it is able to support an adequate amount of materials without much sagging. The mesh size should be big enough for concentrated solutions to go through relatively easily, but not so big as to let carrot cubes pass through. Polyethylene was chosen as belt material, which gave desired results.

4.2 Materials

4.2.1 Selection of Solutes (sucrose - sodium chloride - water system)

As discussed previously, the ternary system of sucrose/sodium chloride/water exhibits unique osmotic effects on plant materials. Besides the fact that this high concentration mixture is achievable and readily available, it also exhibits various preservation effects on the processed plant materials.

Because of the significance of this ternary system, modelling of

the osmotic process on the behavior of plant materials in the sucrose/sodium chloride/water mixture is a good representation of the osmotic process study for the application of commercial dehydration of plant materials, especially for a vegetable process. Furthermore, the physical and thermodynamic properties of this aqueous solution has also been studied in the past few years in the food engineering group at the University of Alberta.

4.2.2 Carrots

For this experiment, carrots of the (*Spartan Fancy*) variety were used. They were provided by I. & S. Produce Ltd, a local fresh food distributor. The carrots were stored at 4°C for about 2 months, because the storage time and temperature have a significant influence on the sugar content, total solids and specific gravity which will affect the initial condition in calculation of chemical potential as a driving force. In order to minimize the variation, standard storage times and temperatures are necessary. In this study, all the carrot roots were stored around 2 months, at 4°C. The nutritional value of carrots are referred to Appendix 1 and average composition is listed in table 8.1.

4.3 Methods

4.3.1 Process Operation

4.3.1.1 Preparation of the System

As shown in Fig 4.1, the operation of the system starts with the preparation of the osmotic solutions. A double-jacketed vessel with an agitator was used to prepare the osmotic solutions. The preparation was in the following sequence. Commercial sodium chloride was weighed first into the double-jacketed vessel, water was added to let all the NaCl dissolve, then the sucrose was weighed, added and mixed. Water mixed with live steam was provided and circulated in the outlayer of the vessel to bring the temperature of the solution to 50°C while the solution was being mixed. 100 kg of osmotic solution were prepared each time and was used for 4 to 6 sets of runs. Four osmotic solutions with different sucrose and NaCl concentrations were prepared. They were 30% sucrose/18% NaCl, 35% sucrose/22% NaCl, 44% sucrose/7% NaCl and 47% sucrose/8% NaCl.

The first collection pan below the spray was filled with a well-mixed solution, the second pan was filled with solution by over-flowing the solution from the first pan and then the third pan was filled from the second. The solution from the third pan was collected and returned to the vessel. Internal flow pumps were connected to facilitate the mixing of osmotic solution.

The system was conditioned for 30 minutes before the carrot was loaded on the belt. After each experiment, the solution in each pan was put back into the vessel and the vessel containing the osmotic solution was stored in the cold room (4°C) for the next day's experiment. All equipment was thoroughly washed with warm water and rinsed with cold water after each experiment.

4.3.1.2 Preparation of the Samples

About 5 kg of carrot roots were taken out each time from the cold room and conditioned at room temperature (23°C) for 2 hours. They were then peeled and diced into cubes approximately 0.85 cm a side using a Hobart cutting machine. The carrot cubes were then sorted with a sieve to remove odd shaped pieces, and weighed (Mo).

4.3.1.3 Operations

When both the system and carrot samples were ready, the carrot cubes were put on the perforated moving belt at the end opposite the entering osmotic solution. The thickness of the layer of carrot cubes on the belt was about 2 cm. As soon as the first carrot cube was at the edge of the third section (nearest to the beginning), the starting time was recorded. As the belt moved, carrot cubes were continuously loaded. The loading rate was measured by the difference in weight of the carrot cubes left after a certain period of time. Similarly the discharge rate was determined by measuring the weight of the discharged carrot cubes over time. After about 30 minutes operation, the process reached steady state (which was tested in the trials and will be discussed in the preliminary study section), and three samples of approximately 60 g each were taken from the end of first section, the middle of the second section and the third section separately. The times were recorded. These samples were rinsed with water and blotted with paper, then put

into a well-sealed containers for analysis. The final carrot cubes discharged from the first section (end of the belt) were weighed (M) and the mass loss was calculated.

The solution samples were collected at the same position on the belt as the carrot samples in order to monitor the concentration changes on the solution side. The osmotic solution at the inlet and outlet of the belt were also collected for each set of experiments. The flow rates of the osmotic solution at the inlet and the outlet were measured by weighing the amount of solution over time periodically. The solution coming from the third collection pan was filtered and put back into the vessel for recycling. Every experiment was conducted twice under the same conditions in order to check the consistency of the process (three replicates for preliminary study).

4.3.2 Equilibrium Study

To estimate the mass transfer driving forces between the surface and the inside material, one requires information on the surface properties of the material. Therefore, an equilibrium study was conducted.

4.3.2.1 Preparation of the Sample

The carrots were conditioned following same procedure than for experiment 4.3.1.2.

4.3.2.2 Sample Treatments

The equilibrium studies were conducted with the following concentrations: 47% sucrose/8% NaCl, 44% sucrose/7% NaCl, 35% sucrose/22% NaCl, 30% sucrose/18% NaCl, 41% sucrose/2% NaCl, 36% sucrose/4% NaCl, 33% sucrose/8% NaCl and 28% sucrose/10% NaCl with three replicates for each.

The first four sets of equilibrium studies were conducted at the same time as the normal runs. For these experiments, the osmotic solutions were taken from the tank which contained the solutions prepared for the operation in the contactor. For the other four sets of studies, the solutions were prepared by blending the required amount of sodium chloride, and sucrose with distilled water on a weight-to-weight basis.

An experiment was conducted in the following manner: approximately 60 grams of carrot cubes were selected, weighed accurately (Mo), and added to a container with 1500 ml of osmotic solution. The ratio of osmotic solution to carrot cubes was large in order to keep the concentration of the osmotic solution relatively constant during the course of the study. Gentle agitation was provided by a magnetic stirrer. The temperature of the container was maintained at 45°C in a water bath for a time duration of 24 hours. A lid was provided for each container to prevent evaporation during treatment. The diagram of the osmotic treatment apparatus is shown on Fig. 4.2.

At the end of the osmotic treatment, the carrot cubes were removed from the vessels, then rinsed quickly in five different beakers

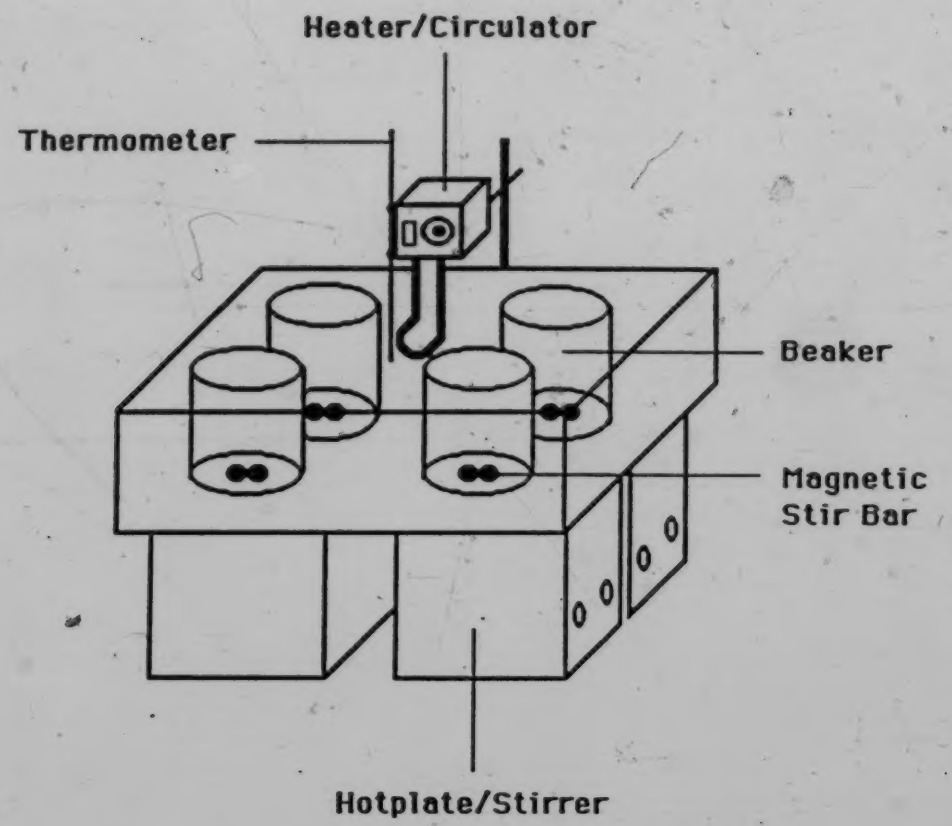

Fig. 4.2 Diagram of the Osmotic Treatment Apparatus for the Equilibrium Study

containing distilled water and gently blotted with paper in order to remove the surface solution. The material was weighed again (M) to calculate the mass loss (ML). Each sampling of carrot cubes both from the contactor and the equilibrium study was divided into three sets for moisture measurement, sugar and NaCl content and density determination (some experiments). The solution samples were collected before and after the osmotic treatments both for the contactor and the equilibrium study to measure changes in concentration.

4.3.3 Measurement of Moisture Content

Each moisture content determination was conducted gravimetrically with a vacuum oven (25 inches Hg, National Appliance Company) at 75 °C for a period of 24 hours.

Some of the treated carrot cubes were ground with a Moulinex blender. About 3 grams of ground carrots were weighed into predried, aluminum foil dishes. The dishes were placed in the oven. After cooling in a desiccator under vacuum, the dishes were reweighed and the moisture content was calculated.

4.3.4 Determination of Sugar and NaCl Content

4.3.4.1 Extraction Procedure

Approximately three grams of blended carrot cubes were weighed in a 50 ml centrifuge tube and 15 ml of 0.5% precooled (at 4°C) H_3PO_4

solution was added. The mixture was homogenized with a Polytron homogenizer for 30 seconds with the content in the centrifuge tube immersed in an ice-bath. After rinsing the Polytron blade with 0.5% H_3PO_4 solution, the slurry was weighed accurately. The samples were centrifuged at 4°C for 20 min. (1700 rpm rotor JA-20, Beckman, Model J-21B). Five mL supernatant were taken, passed filtered through Sep-Pak, and then through millipore paper (0.45 μm). The solutions were ready for HPLC injection both for sugars and sodium chloride analysis (Fig. 4.3 shows the diagram of the extraction).

4.3.4.2 Measurement of Sugar Content

4.3.4.2.1 HPLC System

The HPLC system consisted of a HPLC pump and a Waters Associated model R401 Differential Refractometer (RI) detector maintained at 25°C with a constant temperature ethylene glycol bath. The system was equipped with a 20 μl Rheodyne loop injector. A Bio-Rad Aminex HPX-87N ion exclusion column (300 x 7.8 mm i.d) was used for the separation of sugar. The advantage with this column is that it allows samples to contain a certain amount of salt without interfering with the sugar separation. A heater (BioRad, HPLC Column Heater) was used to maintain the column temperature at 85°C. A 40 x 4.6 mm I.D. guard column was used to protect the main column. A Hewlett Packard 3388A Integrator was attached to RI detector for quantification. The systematic diagram of HPLC system is shown in Fig. 4.4.

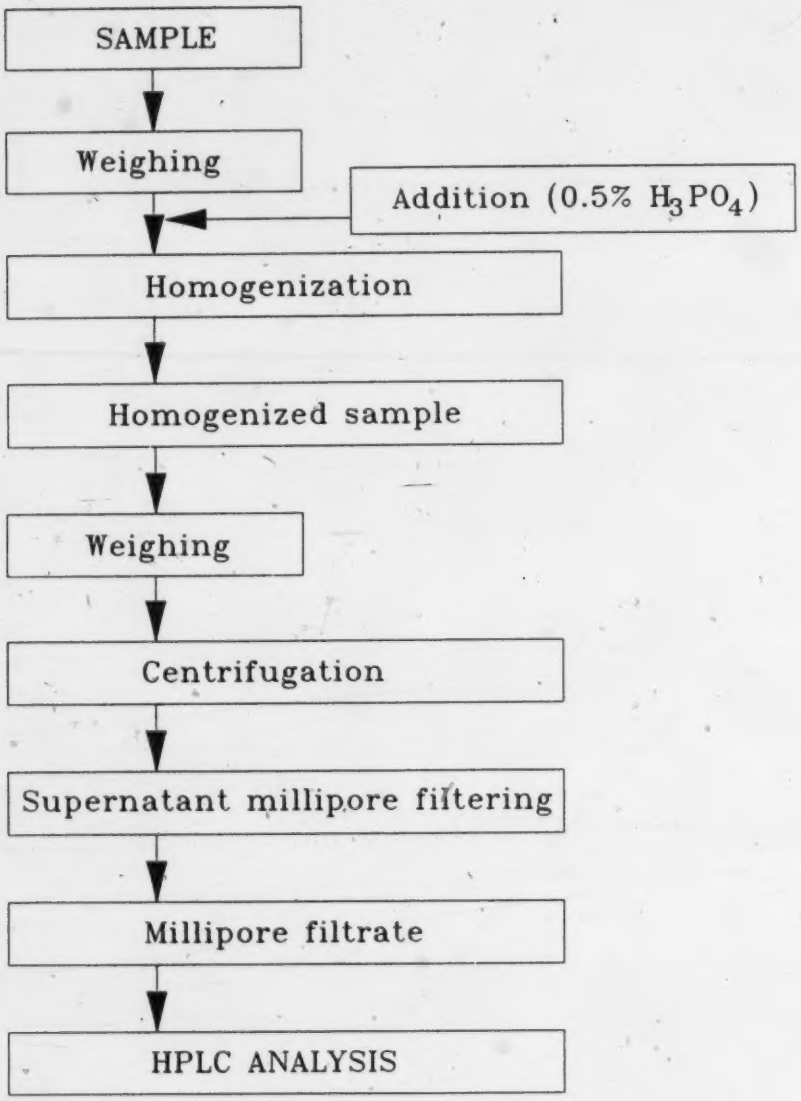

Fig. 4.3 Flow Diagram of Sugar & NaCl Extraction Procedure for HPLC Analysis

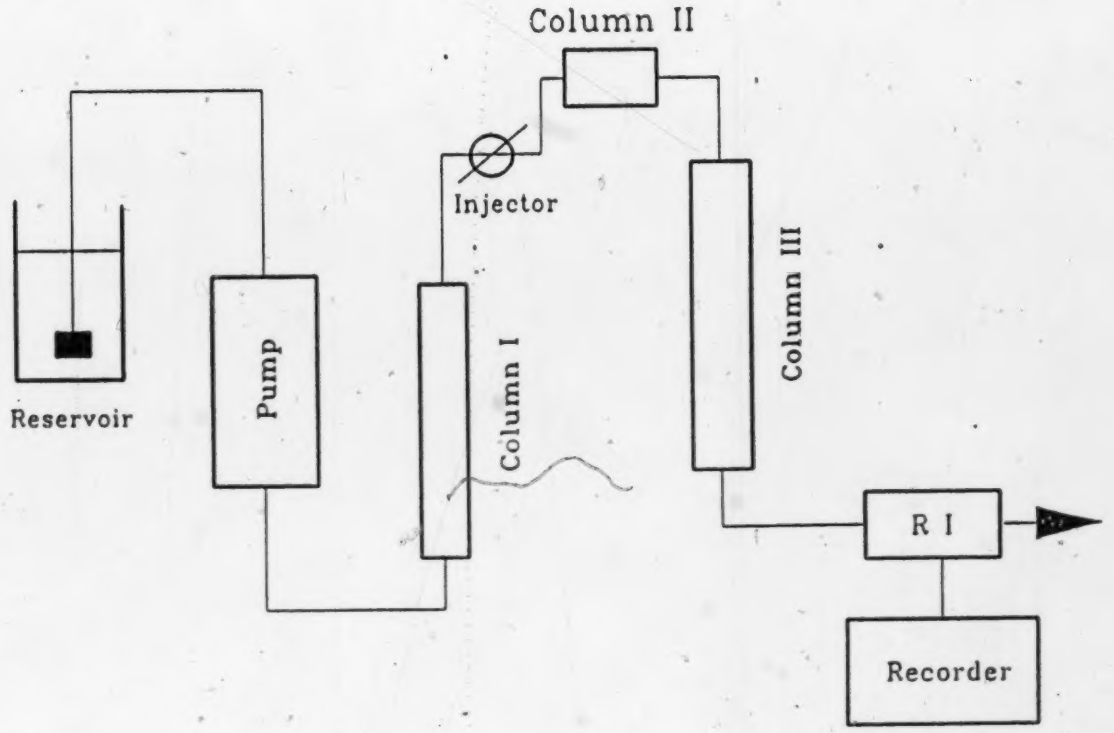

Fig. 4.4 Schematic Diagram of the HPLC System for Sugar and Sodium Chloride Analysis

4.3.4.2.2 HPLC Separation Conditions

The analysis was carried out using an HPX-87N analytical column with the mobile phase of 0.015M Na_2SO_4, PH 5.7, and a flowrate of 0.6 ml/min at 85 °C. The solution was prepared using analytical grade Na_2SO_4 obtained from the Fisher Scientific Company. HPLC grade water was prepared using a reverse osmosis Millipore MIlli-Q system. (Millipore Corp. Bedford,Ma. USA). The solution was degassed and filtered through a 0.45 μm millipore membrane prior to use.

4.3.4.2.3 Analysis

Quantitation was accomplished by preparing a calibration curve with analytical grade sucrose, fructose and glucose(Fluka Chemie AG, CH-9470 Buchs). The weight percentages for each sugar sample were plotted against the peak areas. Calibration involved graphical and statistical determination using simple linear regression. Samples prepared in the extraction procedure were injected into the system. The retention time was around 15 minutes.

4.3.4.3 Measurement of NaCl Content

4.3.4.3.1 HPLC System

The HPLC system consisted of similar components to the sugar

separation system with the exception of an analytical column Whatman 250*4.6 mm I.D Partisil 10, strong anion exchange (SAX). It was protected by a 100x4.6 mm i.d guard column containing the same pellicular ion-exchanger as the analytical column. In addition, a pre-injector 250x4.6 mm i.d precolumn (Solvecon) containing silica gel was attached.

4.3.4.3.2 HPLC Separation Conditions

The mobile phase was 0.017 M potassium dihydrogen phosphate (KH_2PO_4) HPLC grade, prepared fresh daily, dissolved in HPLC water. PH was adjusted to 4.0 with phosphoric acid. The buffer was filtered through Millipore paper (0.45 μm) and degassed prior to use. The mobile phase was used for HPLC analysis with a flowrate of 1.2 ml/min at ambient temperature.

4.3.4.3.3 Analysis

Quantitation was accomplished by preparing calibration curves with analytical grade sodium chloride (Fluka Chemie AG, CH-9740 Buchs). The weight percentage for sodium chloride was plotted against the peak area. Calibration involved graphical and statistical determination using simple linear regression. The extracted samples were injected into the system, and the retention time for the chloride was 13 minutes.

4.3.5 Density Determination

A volume displacement technique was used to determine density. An empty pycnometer was weighed, filled up with distilled water and weighed again, to calculate the volume of the pycnometer. Three carrot cubes were placed in the pycnometer, which was filled up with distilled water, reweighed, and then the density of the carrot cubes was calculated.

4.3.6 Calibration of the Extraction and HPLC Separation Procedure

The osmosed samples were analyzed five times each to determine the precision of the extraction and the analysis procedure. The results are listed in table 4.1 and show a precision of around 3.5% for fructose and glucose, and 2.2% for sodium chloride. In the case of sucrose, less uncertainty is expected.

In addition, the confidence interval on the standard curve for calibration of HPLC separation was constructed. Fig. 4.5 shows a typical sucrose standard curve with 95% confidence limits. It is important to note that the minimum width confidence interval is always obtained around the mean point. Fig. 4.5 gives a general picture of the variation of the estimate. The further a value is away from the mean value, the wider the confidence interval is. Thus, a better estimation appears near the center of the region of experimentation than on the periphery. The simple regression line was constructed every day in order to check the variation from the environment such as the temperature and the mobile phase. Detailed information is listed in Appendix 2.

Table 4.1 Precision of Extraction and Analysis Procedure

Compound	Amount mg/g	Average (mg/g)±SD	% Coefficient of Variance (% CV)
Sucrose	167.22		
	165.99		
	167.72	168.9±2.8	1.7
	170.91		
	172.68		
Glucose	17.47		
	16.57		
	15.98	16.7±0.6	3.6
	16.57		
	17.09		
Fructose	18.00		
	17.62		
	16.82	17.2±0.6	3.5
	16.45		
	16.97		
NaCl	27.72		
	26.73		
	27.29	27.2±0.6	2.2
	26.36		
	27.69		

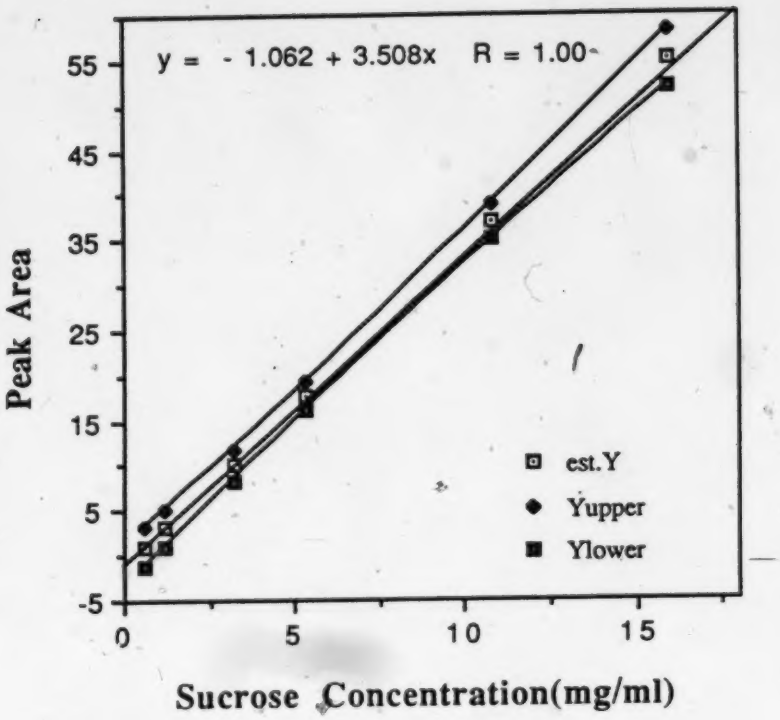

Fig. 4.5 Standard Curve for Sucrose

To further prove the procedure, the average composition of fresh carrots was compared with that in the literature. The average composition of carrot cubes is given in table 4.2. The sucrose, glucose and fructose contents were found to be 5.17±1.48%, 1.14±0.25% and 1.04±0.32% respectively. This finding is in agreement with that of Rygg(1954).

The sodium chloride content in fresh carrots was 0.21±0.09% which is very close to the literature value (Adams, 1975). The average density of fresh carrots was found to be 1.05±0.01 g/cm^3, and the average total solids content of fresh carrot was found to be 12.95±0.56%. All these results are in accordance with the expected values. This indicated that analytical methods are reliable and reproducible.

Table 4.2 Experimental Measurement of Composition of Fresh Carrot Cubes

	Average Percent ±SD	Range Percent ±SD
Total solids (%)	12.95±0.56	12.07 - 13.79
Sucrose (%)	5.17±1.48	3.88 - 6.95
Fructose (%)	1.04±0.32	0.63 - 1.43
Glucose (%)	1.14±0.25	0.82 - 1.43
NaCl (%)	0.21±0.09	0.12 - 0.34
Density (g/cm^3)	1.05±0.01	1.01 - 1.06

5. RESULTS AND DISCUSSION

5.1 General Analysis the Performance of the Contactor

5.1.1. Preliminary Studies

To get the system under control, a series of experiments were conducted to check every part of the system and investigate the parameters of the contactor, such as flow rate (external and internal) of osmotic solution, carrot flow rate, solution temperature, contact time and concentration of osmotic solution.

The experiments were conducted in the following manner: the carrot cubes to be processed were evenly fed manually to one end of the belt. They were discharged at the other end by gravity. The osmotic solution was distributed on top of the carrot cubes and percolated through the bed of solids and the perforated belt. It was then collected in the pans. After filtration, the osmotic solution was pumped and recirculated within its own section while the net liquid flow was obtained by overflow from the collection pans.

The preliminary study was conducted with 60%sucrose solution and 45% sucrose/10% NaCl both at 23°C and 45°C for three complete runs each (three replicates). Total solid content of the samples was measured to evaluate the process. A lot of difficulties were encountered at the beginning of the trials. One of the problems was that all the thin pipes clogged very easily with pieces of carrot and viscous osmotic solution. Improved circulation was achieved by filtering the solution

at the bottom of each pan before internal circulation and at the exit of the solution before recycling back to the solution tank. The trials also revealed that the concentrations and temperature of the osmotic solutions were limiting factors for continuous operation. For this process a 60% sucrose solution at 23°C, even at 45°C, was difficult to pump through. In order to create even conditions for osmotic study, it was decided to keep the temperature at around 45°C for all the experiments. The total solids in the osmotic solution were maintained at around 55% on a weight basis. The variation in temperature among the pans was around 4°C due to exposure to the surroundings and contact with carrots during the process. The results of the trial were stable and reproducible so that two runs (two replicates) are representative enough to justify further experiments.

Preliminary study also showed that the overall flow rate of the osmotic solution at inlet and outlet changed significantly during the process, due to the concentrated solutions. It was found that if the inlet flow rate was lower than 1 kg/min, the variation was larger, therefore an external flow rate of around 1 kg/min was used.

The internal flow rate was chosen according to a packed bed type contactor which was studied in the group. In their experiment, the volumetric flow rate of the osmotic medium was kept at 9 l/min with good dehydration results. Thus, a similar practical internal flow rate was considered in this study. The flow rate of carrot cubes was relatively linear both at inlet and outlet.

Steady-state was also tested with regard to the concentration change at certain positions of the belt. It was demonstrated that after

30 to 50 minutes operation, the carrot cubes had the same concentration at the same position of the contactor and at that point the process was considered to have reached the steady-state. Using this verification, the sampling was made at different positions along the contactor after the process reached steady-state (after approximately 30 minutes) for further experiments.

During the trial, recycling the solution was also investigated using a refractometer to measure changes in total solids. Solids decreased by approximately 1% after two complete sets of experiments, This decrease jumped to about 3.5% after three complete sets. Therefore, the procedure was standardized so that the same solution would be used only for three runs, before being blended with 5 kg of solution with initial concentration for another one or two more runs. Recirculation of the solution will be discussed later.

The preliminary study revealed great advantages in this pilot scale continuous process. These trials have improved the function of the contactor considerably and provided the first information on suitable experimental conditions. Table 5.1 is a summary of planned experiments to be conducted. It should be pointed out that all the experiments were studied with constant temperature around 45^{o}C and fixed internal and external flow rates (8:1). The concentration of osmotic solutions was chosen according to the literature that the mixture of sucrose and salt is most effective in that range (Islam and Flink, 1982). The contact time was controlled by varying the belt speed with a gear box. Based on knowledge from literature, the rate of water loss is maximum at the beginning of the process. Thus it was decided to focus investigations

Table 5.1 Experimental Plan for Mass Transfer Studies

Solution		Contact	Temp.	Replicates
Sucrose (%)	NaCl (%)	Time (min)	(C^o)	
44	7	16	45	2
47	8	16	45	2
35	22	16	45	1
30	18	16	45	2
44	7	55	45	2
47	8	60	45	1
35	22	65	45	1

on a short contact time of around one hour. Two different total contact times were chosen out of four, that is: 16 minutes and 65 minutes.

5.1.2 Osmotic Behavior of Carrot Cubes on a Continuous Process

5.1.2.1 Experimental Measurements

Experimental measurements of the total solids (TS), the sugar content (SUC), and the sodium chloride content (SCC) of carrot cubes at the various contact times on the contactor at an average temperature of 45°C with the different concentrations of sucrose/NaCl mixture are listed in table 5.2.

As shown in table 5.2, A & B; C & D; E & F; H & I were replicates under the same operational conditions with respect to contact time and the concentration of osmotic solutions. T-test (Student's t) showed that there was no significant difference between each replicate in terms of the total solid content (TS), the sugar content (SUC), and the sodium chloride content (SCC)(the highest t=2.02, d.f = 2). This indicates that the performance of the contactor is stable and reproducible.

The final total solids content of the carrot cubes fall within the range of 19% to 36%. The final sugar content in the carrot tubes varies from 11% to 18%. It appears that the concentration of sugar in the osmotic solution does not significantly affect the sugar content during the short contact time provided the total solids in the solution are around 50%. This can be seen from a comparison of treatments A & B and C & D.

Table 5.2 Experimental Measurements of Total Solids (TS), Sugar Content (SUC) and Sodium Chloride Content (SCC) of Carrot Cubes at Various Contact Time on the Contactor at an Average Temperature of 45°C.

	Solution		Contact Time	Total Solids	Sugar Content	NaCl Content
	Sucrose (%)	NaCl (%)	(min)	(TS) (%)±SD	(SUC) (%)±SD	(SCC) (%)±SD
A	30	18	16	24.24±0.07	12.72±0.40	5.41±0.39
B	30	18	16	24.98±0.34	11.33±0.54	5.95±1.20
C	44	7	16	19.77±0.86	12.28±0.54	1.10±0.14
D	44	7	16	20.35±0.18	12.28±0.82	1.55±0.52
E	47	8	16	22.52±0.08	13.93±0.56	1.48±0.40
F	47	8	16	22.70±0.10	12.87±0.76	1.29±0.68
G	35	22	16	25.95±0.13	13.82±1.51	6.81±2.67
H	44	7	55	23.99±0.21	16.56±2.56	1.76±0.51
I	44	7	55	24.28±0.19	14.49±1.70	1.67±0.24
J	47	8	60	29.60±0.08	18.85±0.72	2.89±0.80
K	35	22	65	36.41±0.18	18.42±0.41	11.05±1.28

The sodium chloride content varied from 1.1% to 11.05%. The difference in sodium chloride content is primarily due to its concentration in the osmotic solutions. High concentrations of sodium chloride in an osmotic medium resulting in a high sodium chloride content in the products. It appears that the NaCl concentration in the osmotic solution has an impact not only on the salt content, but also on the sugar content of final products. Probably, that the addition of salt lowers the viscosity of a solution, and the salt may have a significant effect on the cell wall or membrane properties.

5.1.2.2 Transformation into Typical Osmotic Parameters

5.1.2.2.1 Calculation of Osmotic Parameters

In order to describe the mass transport phenomena in the osmotic process, the following terminology has been used to indicate the overall exchange of solutes and water between the materials and the osmotic solution: Mass Loss (ML), Water Loss (WL), Sugar Gain (SUG), and Salt Gain(SCG).

As described by Lenart and Flink (1984a), the mass loss (ML) or weight loss can be defined as the net loss in weight of the carrot cubes on an initial carrot cube weight basis.

$$ML = \left[\frac{M - Mo}{Mo}\right] \times 100\% \qquad [5.1]$$

The water loss (WL) is the net loss of water from carrot cubes on

an initial carrot weight basis and is calculated from the mass of carrot after osmotic treatment (M), initial mass (Mo), weight fraction of total solids in the carrot cubes at initial (W^o_{ts}), and weight fraction of total solids in the carrot cubes after osmotic treatment (W_{ts}):

$$WL = \left[\frac{M_w - M^o_w}{M_o} \right] \times 100\% \qquad [5.2]$$

Since $$M_w = M\ (1 - W_{ts}) \qquad [5.3]$$

$$M^o_w = M_o\ (1 - W^o_{ts}) \qquad [5.4]$$

Thus $$WL = \left[\frac{M\ (1-W_{ts}) - M_o(1-W^o_{ts})}{M_o} \right] \times 100\%$$

$$= \left[\frac{M}{M_o}\ (1 - W_{ts}) - (1 - W^o_{ts}) \right] \times 100\% \qquad [5.5]$$

Sucrose gain and sodium chloride gain are defined as the net uptake of sucrose and sodium chloride by the carrot cubes based on the initial weight of carrot cubes. They are functions of the mass reduction ($\frac{M}{M_o}$), the initial weight fractions of sugar or NaCl (W^o_{su}, W^o_{sc}) and after the treatment (W_{su}, W_{sc}).

That is

$$SUG = \left[\frac{M_{su} - M^{o}_{su}}{M_{o}} \right] \times 100\% \qquad [5.6]$$

or

$$SUG = \left[\frac{M}{M_{o}} W_{su} - W^{o}_{su} \right] \times 100\% \qquad [5.7]$$

Similarly,

$$SCG = \left[\frac{M_{sc} - M^{o}_{sc}}{M_{o}} \right] \times 100\% \qquad [5.8]$$

$$SCG = \left[\frac{M}{M_{o}} W_{sc} - W^{o}_{sc} \right] \times 100\% \qquad [5.9]$$

5.1.2.2.2 M/Mo Calculation

The M/M_{o} is obtained on the conservation of total insoluble solids i.e.

$$\frac{M}{M_{o}} = \frac{W^{o}_{in}}{W_{in}} \qquad [5.10]$$

The detailed description of M/Mo is illustrated in Appendix 4.

5.1.2.2.3 Results

These osmotic parameters, such as mass loss (ML), water loss (WL), sugar gain (SUG) and sodium chloride gain (SCG) at different contact times were calculated. The propagated error calculation is illustrated in Appendix 5. The results are listed in table 5.3 at various contact times together with the propagated errors.

The mass loss (ML) was within the range of 21% to 36%. Mass loss (ML) is very sensitive to the change of contact time and the concentrations of osmotic media. The highest mass loss (36%) was observed with 35% sucrose/ 22% NaCl for 65 minutes contact time.

The water loss (WL) was in the range of 25.8% to 46.3%. The highest water loss was also found with 35% sucrose/22% NaCl solution for 65 minutes contact time. This is undoubtedly due to the lowering capability of water activity by NaCl, thus increasing the driving force of mass transfer at the beginning. Another reason is that this treatment was associated with a longer contact time than any other treatments under investigation.

Analysis of sugar gain indicated that sugar gain is not proportional to sugar concentration in the osmotic solution when the contact time is short. The highest sucrose gain was in the final product (around 6.6%) and was found using the 47% sucrose/8% NaCl solution, with 60 minutes contact time. The effect of longer contact time with a high sucrose concentration in the osmotic solution resulted in a high sugar gain. Sugar gain varied from 1.8% to 6.6%.

Unlike sugar gain, sodium chloride gain was higher both at 16 minutes and 65 minutes with high sodium chloride concentrations in the

Table 5.3 Calculated Parameters: Mass Loss (ML), Water Loss (WL), Sugar Gain (SUG), Sodium Chloride Gain (SCG) and Soluble Solids Loss (SSL) of Carrot Cubes at Various Contact Time with an Osmotic Solution on the Contactor at an Average Temperature of 45°C.

Solution			Contact Time	Mass Loss (ML)	Water Loss (WL)	Sugar Gain (SUG)	NaCl Gain (SCG)	Soluble Solids Loss
	Sucrose (%)	NaCl (%)	(min)	(%)±SD	(%)±SD	(%)±SD	(%)±SD	(%)
A	30	18	16	24.03±0.34	29.68±0.43	3.19±0.74	3.89±0.33	1.43
B	30	18	16	26.70±0.21	32.94±0.50	1.80±0.45	4.21±0.88	0.23
C	44	7	16	23.66±0.37	25.80±0.20	2.22±0.45	0.62±0.35	0.70
D	44	7	16	24.49±0.23	27.43±0.50	2.12±0.79	0.95±0.31	0.13
E	47	8	16	23.03±0.49	26.80±0.13	2.76±0.49	0.87±0.57	0.14
F	47	8	16	23.69±0.47	27.32±0.58	2.73±0.66	0.86±0.68	0.04
G	35	22	16	21.56±0.51	29.54±0.74	2.61±1.77	5.22±1.50	0.15
H	44	7	55	28.70±0.45	32.83±0.66	5.18±1.42	1.14±0.93	2.19
I	44	7	55	28.55±0.52	33.53±0.83	4.73±1.37	1.07±0.78	0.82
J	47	8	60	23.68±0.43	31.11±0.62	6.56±0.72	1.86±0.63	0.99
K	35	22	65	36.31±0.40	46.26±0.67	3.51±0.78	6.82±1.67	0.38

solution (treatments A & B, G and K). A longer contact time also contributes a high salt gain. This is shown by comparing treatments E&F and J (Table 5.3) which used the same concentration of osmotic solution but different contact times. It appears that the salt concentration in the osmotic solution has a greater effect on the uptake of solids. Salt penetrates readily into carrot tissue. The membrane does not seem to offer a significant resistance to the passage of the solute.

The osmotic behavior of carrot cubes in sucrose and NaCl solutions showed the basic difference between these two solutes. The small molecule of the salt ion can more easily diffuse through the cell membrane resulting in high NaCl gain even with a very short contact time. As Toupin (1986) described, the main reason for the observed responses resides in the effective permeability of the membrane to this diffusible solute which literally opens the whole structure to mass transfer. Sucrose molecules, on the other hand, are larger and the cell membrane is impermeable to this solute. Thus, with very short contact time, only water flow occurs with an insignificant marginal uptake of sucrose. Fig 5.1 illustrates a clear picture in respect to water loss, sugar gain and NaCl gain at 16 minutes with different solutions.

The purpose of osmotic dehydration is to maximize the water loss while minimizing solute gain. If we take the ratio of water loss to solid gain(sugar + NaCl) as an objective function to evaluate the optimum process conditions (Table 5.4), the highest ratio of water loss to solid gain lies at 44% sucrose/7% NaCl at 16 minutes. The ratio is also significant with 47% sucrose/8% NaCl at 16 minutes. Hawkes and Flink (1978), Lenark and Flink (1984a) recommended that 40% sucrose/10%

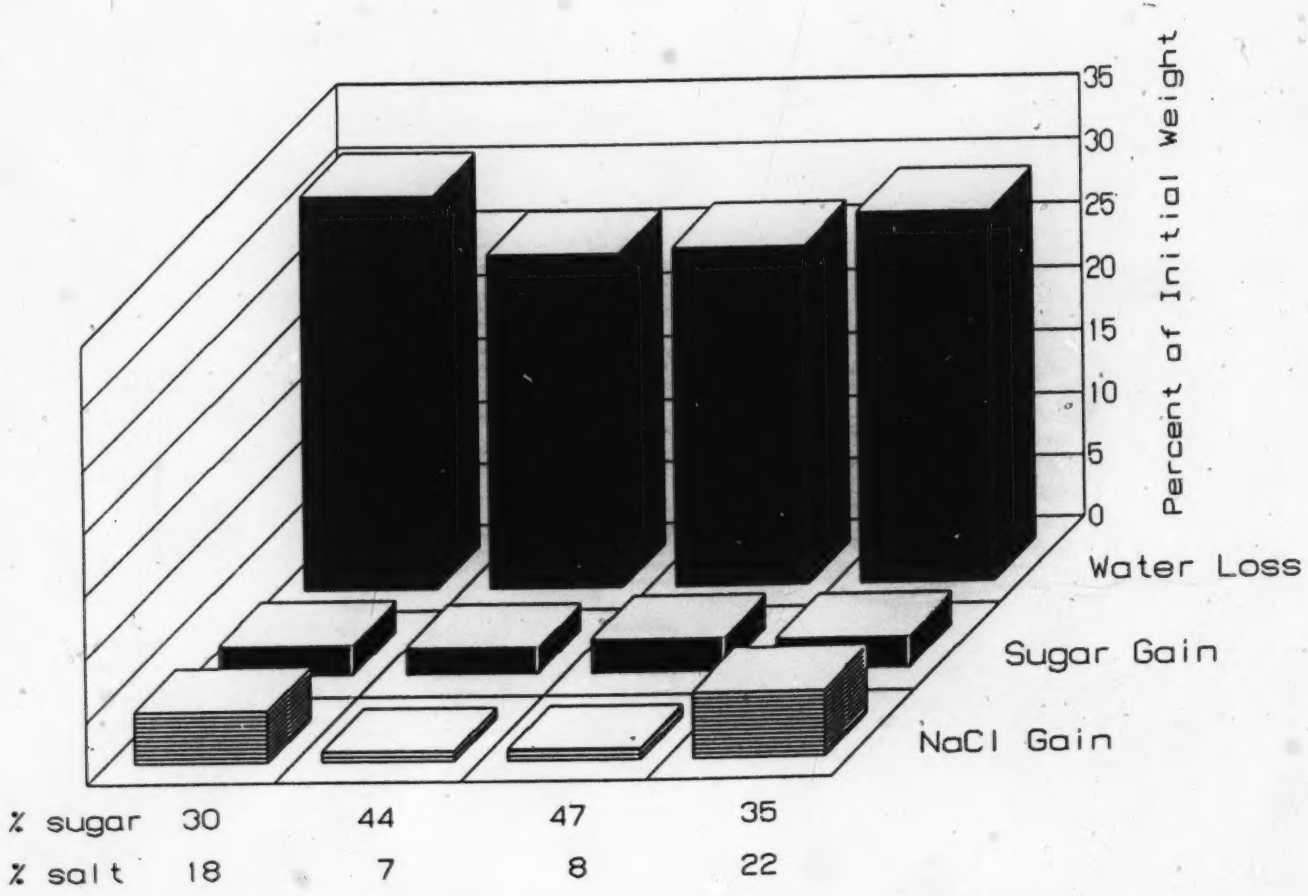

Fig. 5.1 Histogram of Water Loss, Sugar Gain and NaCl Gain for Various Osmotic Medium (16 min Contact)

Table 5.4 Ratio of Water Loss to Solids Gain (Sugar + NaCl)

Treatment	Contact Time(min)	Solution Sucrose	Solution NaCl	Water Loss / Solid Gain
A	16	30	18	4.19
B	16	30	18	5.48
C	16	44	7	9.08
D	16	44	7	8.93
E	16	47	8	7.38
F	16	47	8	7.61
G	16	35	22	3.77
H	55	44	7	5.19
I	55	44	7	5.78
J	60	47	8	3.69
K	65	35	22	4.48

NaCl or 45% sucrose/5% NaCl are the most effective and practical osmotic media. A great difference in chemical potential difference is generated under these conditions resulting in quick water removal. This is also in agreement with statements of a number of researchers that water loss is maximum within the first half hour in batch systems. Again, for the osmotic process both water loss and solids gain play an important role.

Osmotic behavior for short times is also primarily a surface-area related transport phenomemon. This contactor has a relatively larger contact surface beween the osmotic solution and the carrot cubes providing better mass transfer conditions compared with the fixed bed in batch systems. For a short osmotic time, size and geometry of materials have considerable influence on the extent of dehydration as well. A cube with 0.85 cm side is commonly used in current commercial production of carrots. Furthermore, the large amount of osmotic solution provides a relative constant concentration on the solution side which means high chemical potential difference was maintained during the process. The driving force is relatively constant compared with a batch system where the driving force decreases through the process. This may be one of the reasons responsible for fast water removal.

Another significant feature of this process is the effectiveness of the sucrose/salt solution. According to Lenart and Flink (1984b) the effect of additional salt in sucrose is similar to that obtained by a increasing osmosis temperature. This mixture hinders the formation of the compacted surface layer which limited the water removal caused by high sucrose concentration medium alone. Salt also has a significant effect on the cell wall or membrane properties. The behavior in the

sucrose/NaCl mixture exhibits a resistance to the diffusion of salt into carrot tissue due to the presence of sugar. Lenart and Flink (1984b) found that the salt concentration at each location in the potato sample was lower for the 45% sucrose/15% salt mixture than for the 15% salt alone. Furthermore, the sucrose/salt mixture improved rates of water loss. To control processing time as short as possible in order to get maximum efficiency is a goal of commercial production.

The choice of concentration of osmotic medium depends on many factors. The most critical concern is the uptake of salt in the final products. The value found in the treatment in 44%sucrose/7%NaCl solution are comparable to levels of salt in canned products and for remanufactured items such as soup which would allow higher salt content.

5.1.2.2.4 Testing the Hypothesis

As mentioned, the hypothesis is based on the soluble solids conservation during the course of the osmotic process. Because the simultaneous water loss and solids uptake are taking place in an osmotic process, the leaching of soluble solids may be expected. Testing of the hypothesis was done as follows: since, the mass of carrot at time t could be calculated from total mass balance:

$$M = M_w + M_{su} + M_{sc} + M_{ss} + M_{in} \qquad [5.11]$$

initial mass of carrot

$$M_o = M_w^o + M_{su}^o + M_{sc}^o + M_{ss}^o + M_{in}^o \qquad [5.12]$$

Because $M_{in} = M_{in}^o$

Combine Eqs. [5.11] and [5.12]:

$$\frac{ML}{100} = \frac{WL}{100} + \frac{SUG}{100} + \frac{SCG}{100} + \frac{SSL}{100} \qquad [5.13]$$

From Table 5.3, the average soluble solids loss was $\overline{0.60 \pm 0.7}$% in operational conditions. Compared to an initial total soluble solids (non-sugar, non-salt) around 3.9%, we may conclude that the assumption (that is: SSL=0) is valid during short time conditions. It will be interesting in further study to take soluble solid loss into consideration in the future modeling.

5.1.3 Concentration Profile along the Contactor

Total solids content, sugar content and sodium chloride content along the contactor at a total contact time of 16 minutes are listed in Appendix 3. A typical example is plotted against the length of contactor in Fig 5.2.

As shown in Fig. 5.2, total solids increase dramatically at the beginning of the contactor and has linearly increase along the remaining two thirds of the contactor. A similar trend was found in all experiments. It is obvious that higher concentrations of NaCl in osmotic solutions result in a higher total solids uptake due to the penetration of sodium chloride during the process. A similar change in

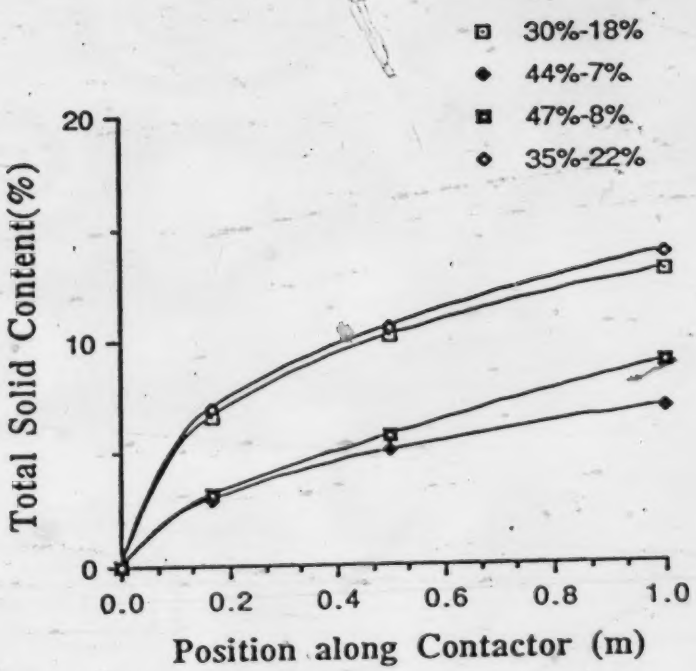

Fig. 5.2 Concentration Profile of Total Solids Content along the Contactor

the sodium chloride concentration profile along the contactor was found. The NaCl content is proportional to the concentration of NaCl in the solution.

The total solids (TS), sugar content (SUC) and sodium chloride content (SCC) profiles of carrot cubes at various concentration are listed in Appendix 3. Knowing the characteristics of concentration change of the carrot cubes along the contactor is essential for simulating and designing an osmotic dehydration process.

5.1.4 M/M_o, M_w/M_o, M_{su}/M_o and M_{sc}/M_o Presentation

5.1.4.1 Curve Fitting

In order to present and interpret the data for a continuous process, the ratios of M/M_o, M_w/M_o, M_{su}/M_o and M_{sc}/M_o have been used as a dimensionless index to take into account that experimental limitations of a continuous process. These parameters were calculated according to the method described in Appendix 4. Experimental data on the reduction in the mass of carrots ($\frac{M}{M_o}$), the reduction of water in carrots ($\frac{M_w}{M_o}$), increase in sucrose and sodium chloride ($\frac{M_{su}}{M_o}$) and ($\frac{M_{sc}}{M_o}$) at 45°C were fitted using one of the following equations.

$$y = A + (y_o - A) e^{-Ct} \qquad [5.14]$$

$$y = y_o + A (1 - e^{-Ct}) \qquad [5.15]$$

In the above equations, y is the dependent variables (M/M_o, M_{su}/M_o, M_w/M_o and M_{sc}/M_o), t is the independent variable (time), y_o is the initial value of y at t=0, and A and C are parameters.

These nonlinear exponential functions have been fitted for M/M_o, M_w/M_o, M_{su}/M_o, and M_{sc}/M_o for all the different working conditions. Eq. [5.14] and Eq. [5.15] are extended as following:

$$\frac{M}{M_o} = A_m + (1 - A_m)\, e^{-C_m t} \qquad [5.16]$$

$$\frac{M_w}{M_o} = A_w + (A_w^o - A_w)\, e^{-C_w t} \qquad [5.17]$$

$$\frac{M_{su}}{M_o} = A_{su}^o + A_{su}(1 - e^{-C_{su} t}) \qquad [5.18]$$

$$\frac{M_{sc}}{M_o} = A_{sc}^o + A_{sc}(1 - e^{-C_{sc} t}) \qquad [5.19]$$

From Eqs. [5.16] and [5.17]

when t=0

$$\frac{M}{M_o} = 1$$

$$\frac{M_w}{M_o} = A_w^o = \frac{M_w^o}{M_o}$$

where 1 is the ratio of initial mass and M_w^o / M_o is the ratio of initial water mass over total initial mass.

From Eqs. [5.18], [5.19]

when t = 0

$$\frac{M_{su}}{M_o} = A_{su}^o$$

$$\frac{M_{sc}}{M_o} = A_{sc}^o$$

where A_{su}^o is the ratio of initial sucrose mass over total initial mass and A_{sc}^o is the ratio of initial NaCl mass over total initial mass.

Generally, the parameter estimation is regarded as an optimization procedure. The least square method was employed to optimize the parameters, where the objective function is the sum of squares of residuals, i.e.

$$S^2 = \Sigma_i (Y^{exp} - Y^{pred})^2$$

The Statistical Analysis System (SAS) was used to estimate the parameters in the equations at each condition. A and C are parameters obtained through non-linear curve-fitting. Table 5.5 is the summary of the estimates of A and C along with their standard errors.

Table 5.5 Optimized Parameter of A and C for $\frac{M}{M_o}$, $\frac{M_w}{M_o}$, $\frac{M_{su}}{M_o}$ and $\frac{M_{sc}}{M_o}$ Through Curve Fitting

	Solution			
	Sucrose (%)	NaCl (%)	A	C
$\frac{M}{M_o}$	44	7	0.692±0.017	0.061±0.008
	47	8	0.694±0.006	0.070±0.004
	35	22	0.552±0.044	0.033±0.007
	30	18	0.834±0.002	0.149±0.005
$\frac{M_w}{M_o}$	44	7	0.526±0.023	0.060±0.010
	47	8	0.491±0.018	0.063±0.007
	35	22	0.324±0.033	0.035±0.004
	30	18	0.577±0.011	0.095±0.007
$\frac{M_{su}}{M_o}$	44	7	0.042±0.002	0.062±0.009
	47	8	0.073±0.009	0.028±0.006
	35	22	0.044±0.006	0.028±0.007
$\frac{M_{sc}}{M_o}$	44	7	0.009±0.000	0.119±0.008
	47	8	0.023±0.002	0.027±0.004
	35	22	0.072±0.005	0.040±0.006

An optimum can be indicated by a comparison of the predicted values with experimental values through some statistics such as RMSD or %RMSD (% root mean square of deviation). Usually, the standard errors of the parameters indicate how well the parameter value is located.

As can be seen in Fig. 5.3 to Fig. 5.6., the curves fit the experimental data very well. The method was found to be reliable and effective in evaluating A and C. From good fitting of the exponential function, with the small standard error of A and C, a good estimate of A and C for all the conditions examined here was obtained.

5.1.4.2 M/M_o, M_w/M_o, M_{su}/M_o and M_{sc}/M_o as a Function of Time and Concentration

Fig. 5.3 illustrates a typical M/M_o as a function of time and concentration. It can be seen that the reduction of mass exhibited an exponential function with contact time. Apparently, in all cases, the rate of reduction is highest during the initial stages of osmotic treatment. At the end of the treatment, the rate of mass reduction decreased as evidenced by the flattening of the curves. These results qualitatively agree with those obtained by other workers employing sucrose or sucrose-NaCl mixture as an osmotic agent.

The effect of osmotic concentration on M/M_o can be illustrated by comparison of the three lines illustrated in Fig 5.3. The treatment with the 35% sucrose / 22% NaCl solution resulted in a sharp decrease in the mass reduction compared with the treatments of 44% sucrose/7% NaCl and 47% sucrose/8% NaCl solutions. This is probably due to the high

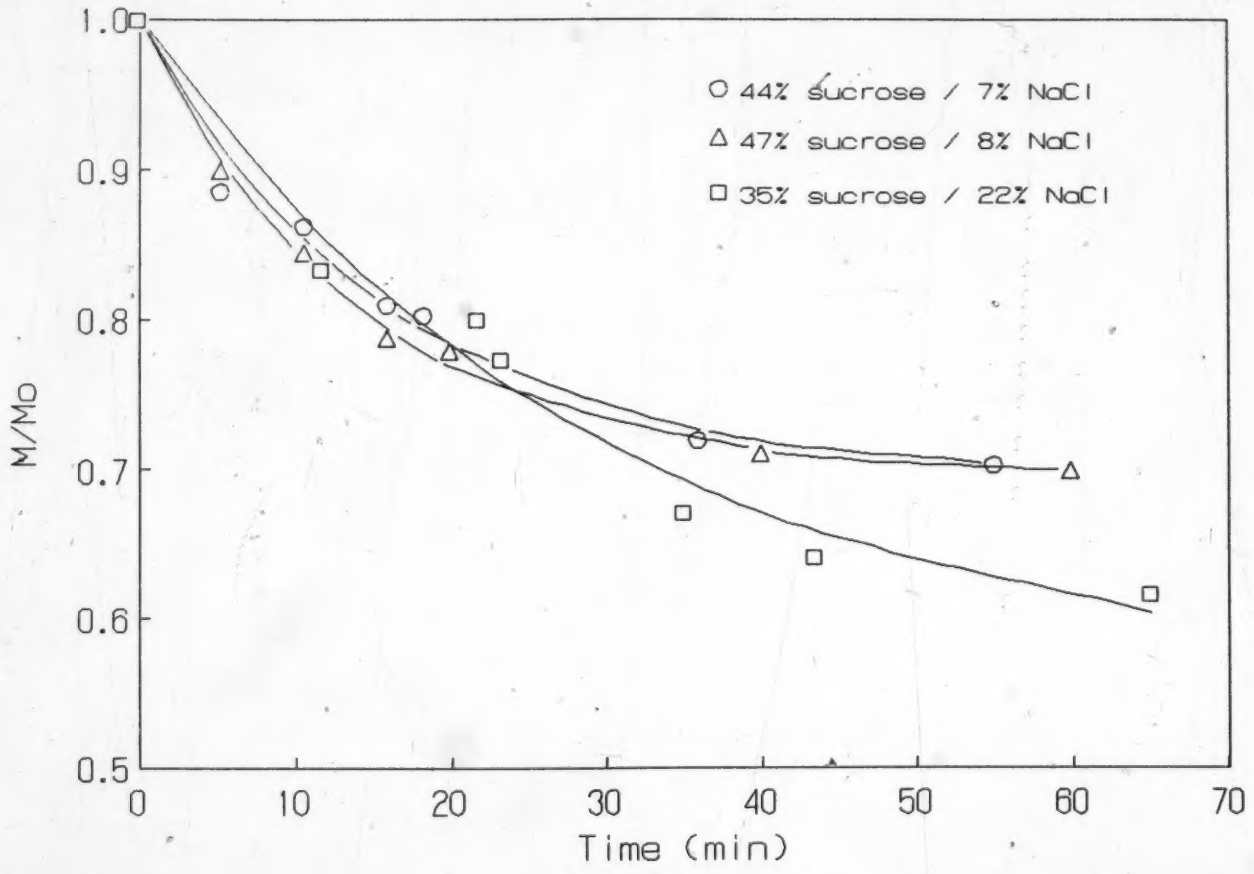

Fig. 5.3 M/Mo as a Function of Time and Concentration

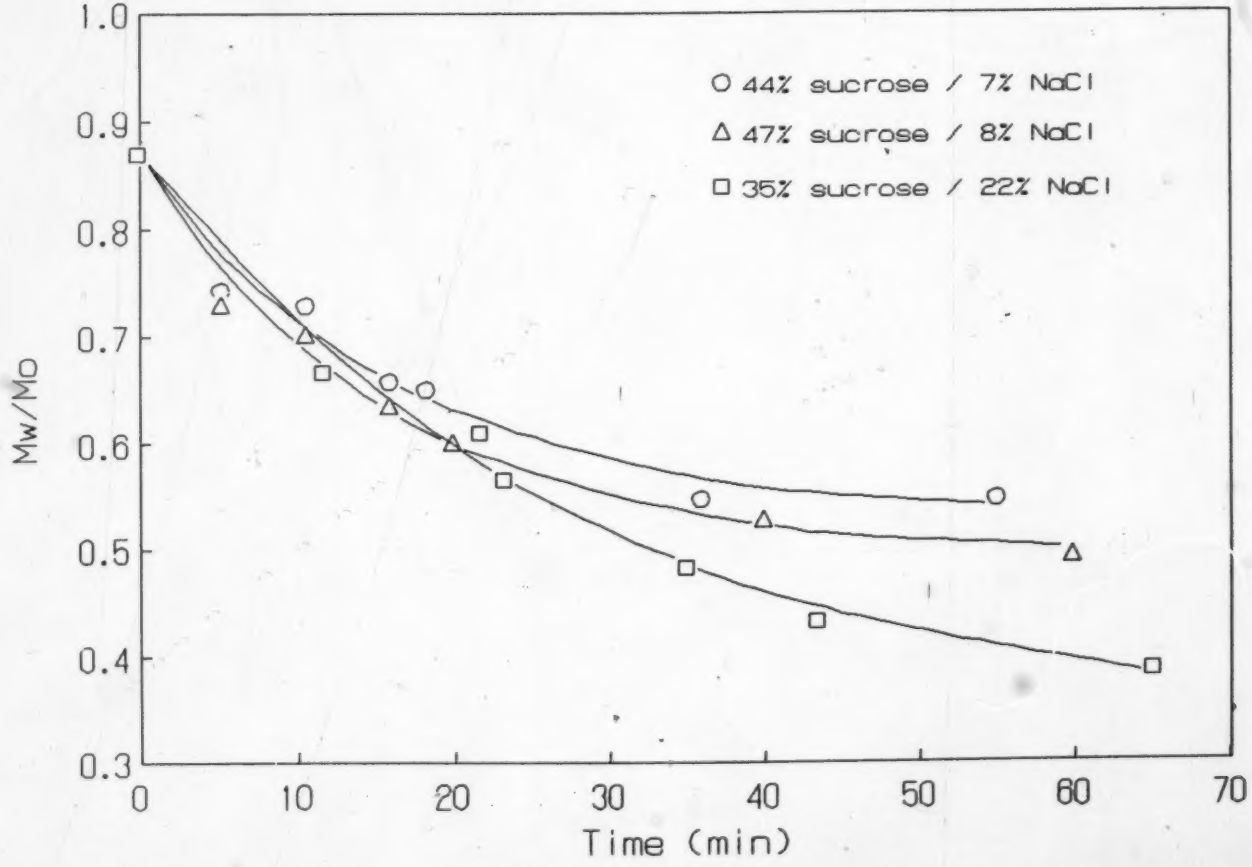

Fig. 5.4 Mw/Mo as a Function of Time and Concentration

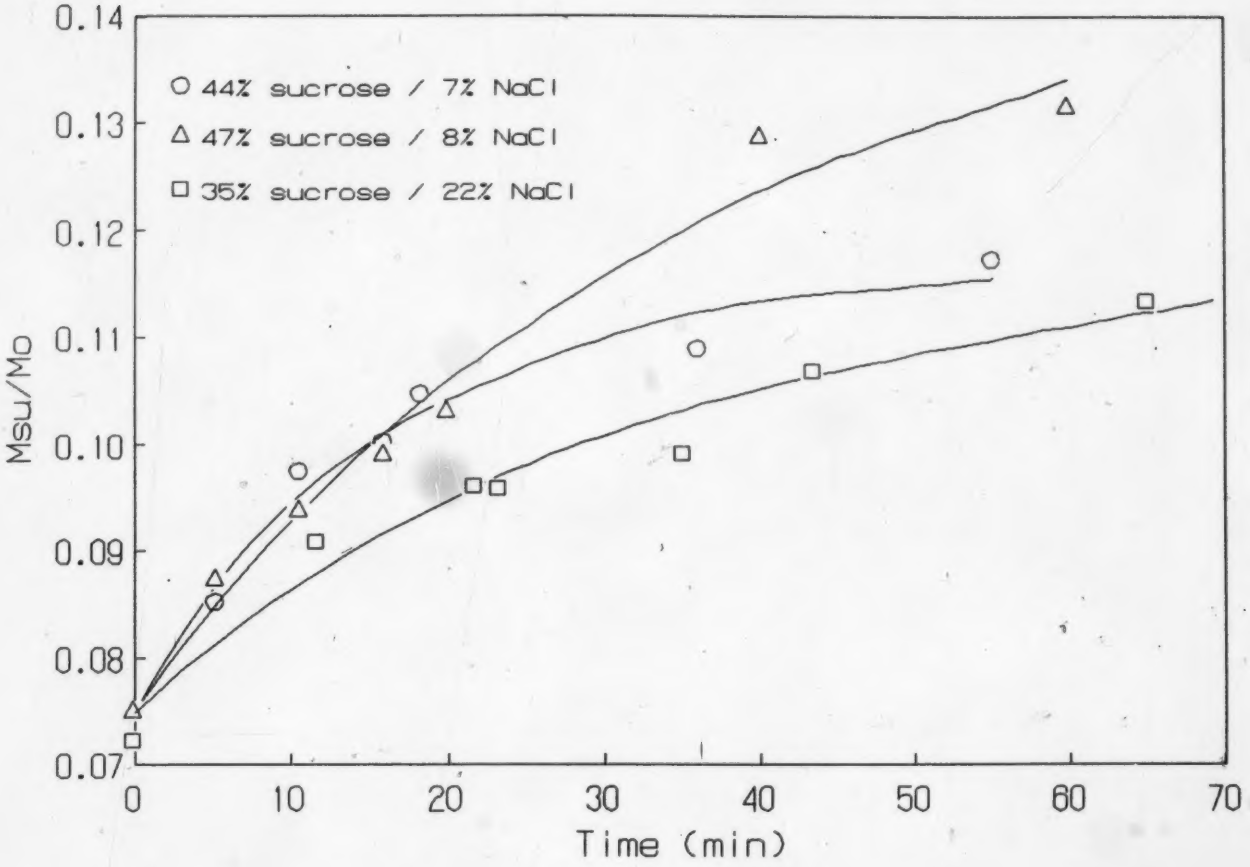

Fig. 5.5 Msu/Mo as a Function of Time and Concentration

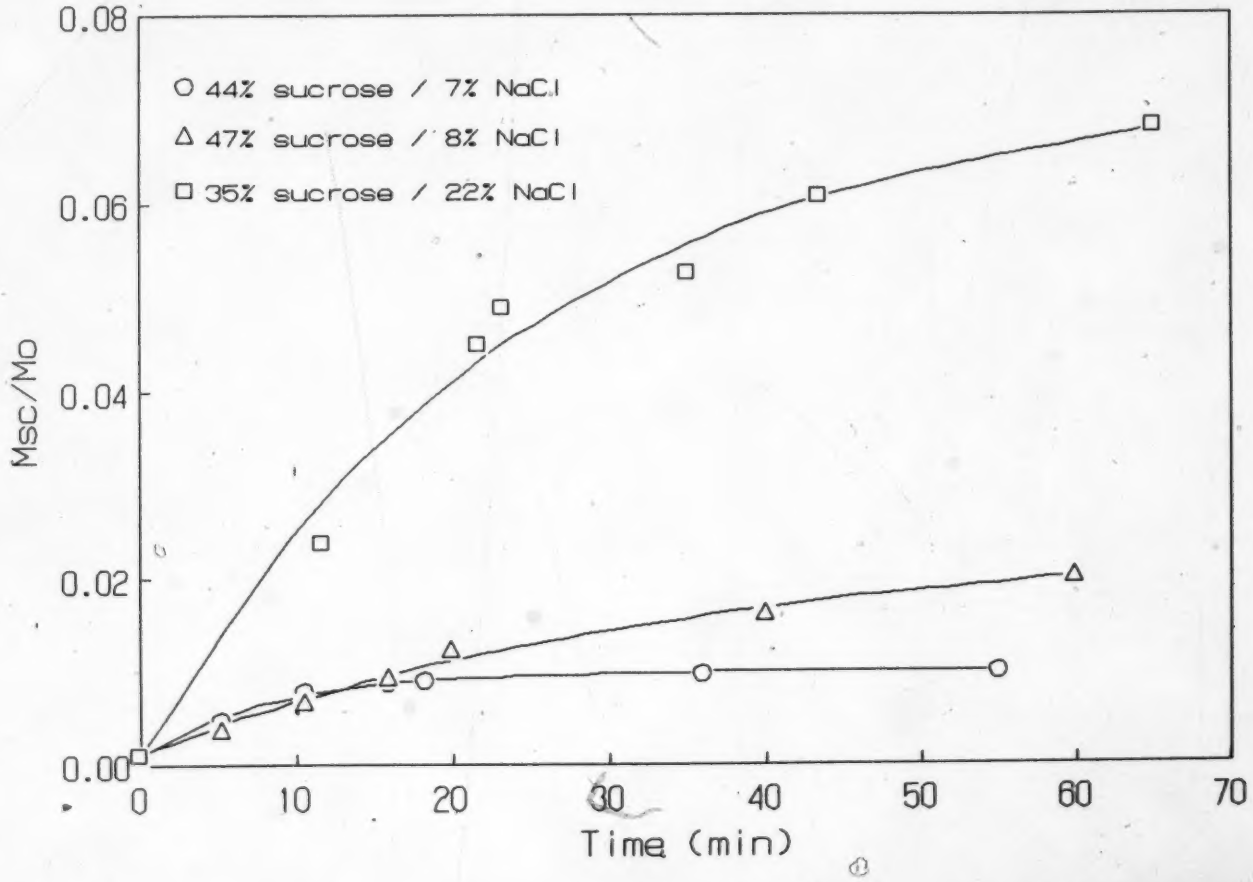

Fig. 5.6 Msc/Mo as a Function of Time and Concentration

total solids concentration in the osmotic solution. A similar trend has been found with M_w/M_o as shown in Fig. 5.4. The ratio of water reduction decreased rapidly within 16 minutes for all treatments, but as contact time increased, the discrepancy between them became larger. The high total solids concentration in the osmotic solution resulted in a high water loss.

From Figures 5.3 and 5.4, it seems that the curves approached equilibrium after about 1 to 2 hours operation. The dramatic reduction in the time for equilibration is due to the combination effect of permeable and impermeable solutes.

The influence of the osmotic concentration and contact time on the sugar uptake of carrot cubes is shown in Fig. 5.5. It can be seen that the ratio of sucrose uptake increases as sucrose concentrations in the osmotic solution increases. It increases very quickly at the outset, then slows down when approaching equilibrium. The longer the contact time, the bigger the discrepancy between the different solutions.

Large difference could be found in the sodium chloride uptake as indicated in Fig. 5.6. The sodium chloride uptake is directly proportional to its concentration in the osmotic solutions. The treatment with 35% sucrose/22% NaCl solution resulted in a 3 or 4 times higher NaCl gain compared with the treatments for 44% sucrose/7% NaCl and 47% sucrose/8% NaCl solutions, respectively. The uptake of individual permeable components in a mixed solution reflects the component concentrations present in the mixed solution. Similar results have been found by Hawkes and Flink (1978). For salt osmosis, this would result in decreased cellular dehydration, thus giving less

shrinkage, increased solute uptake and higher transport properties.

As mentioned previously, the optimum concentration of an osmotic solution with a sugar/salt mixture depends on many factors. However, a higher concentration of an osmotic solution would result in greater difference in chemical potential, thus permitting faster water removal. The optimization of the osmotic solution in terms of concentration remains an important aspect of an osmotic treatment. From the osmotic behavior of carrot tissue under these conditions, all the concentration used are effective. In the case of vegetable processing, 5%-10% NaCl concentration in an osmotic solution would result in a fast water loss, reduction in the cost of the osmotic medium, and also have some taste advantages.

Effects of contact time on M/M_o, M_w/M_o, M_{su}/M_o and M_{sc}/M_o are obvious. Increased contact time will increase reduction of mass (M/M_o), reduction of water (M_w/M_o), increase in sucrose gain (M_{su}/M_o) and NaCl gain (M_{sc}/M_o). However, the rates of these reductions and increases are decreased as time increases. It can evidently be seen in Fig 5.3, Fig. 5.4, Fig. 5.5 and Fig. 5.6. For this reason, all experiments were conducted within 1 hour. Based on practical considerations, it may not be necessary to extend the time beyond one hour in the case of continuous osmotic dehydration for vegetables in a sucrose/salt solution. Contact time may vary from product to product according to the organoleptic requirements of final products and the efficiency of processes.

5.1.5 Recirculation of Osmotic Solution

Recirculation of osmotic solutions is one of the most important aspects so far as commercial application is concerned. In the early stage of the experiment, the osmotic solution was tested after it was reused for one, two, three, four and five runs respectively. Filtering with a sieve was made after the third collecting pan before the solution was recirculated back to the reservoir. It was found that concentrations of the sucrose and NaCl in the osmotic solutions remained relatively constant after the second run because the ratio of solution to the carrot cubes was large. Relatively small amount of solids uptake and water loss did not significantly affect the solution concentration. However, after the third runs, 2.5% sucrose and 1 % NaCl decrease in the solution compared with initial concentrations was found. Evaporation or sterilization at 100°C with live steam for 2 minutes, resulted in 1% increase in total solids concentration in the solution.

An attempt to recirculate osmotic solutions has demonstrated some operational problems. After recirculating five times, a yellowish color was observed in the solution due to carotenoid leaching out from carrot cubes in the third collecting pan where the osmotic solutions were in direct contact with fresh carrot cubes. The color difference was not observed in other pans or in the tank. Increased overall solution circulation by increasing the external flow rate could reduce this discrepency. Solution foaming was observed in the third pan after five runs. This may be because some soluble solids, such as protein, leached out from the carrot cubes. When a high internal circulation of osmotic solution was conducted, the solution dripped down, impacting lower

solution and thus causing the foaming. The dripping speed of the solution may be reduced by decreasing the distance between the belt and the collecting pans, thus reducing the foaming.

In order to have consistent pilot-plant test condition for the study, it was decided that the emphasis at the beginning stage should be upon evaluating the performance of the contactor. Therefore, every 100 kg of osmotic solution was used for 3 runs, then blended with 5 kg of new mixed solution with the same concentration for another one run or two runs if necessary. Nevertheless, the maximum recirculation was five times. New way of defoaming the solution is needed in order to circulate the solution more times. In a commercial operation, the osmotic solution should be used for more runs, since pilot-plant studies concentrated on reducing some variations due to the test condition for the osmotic behavior of materials.

5.1.6 Some Observations Occurring During the Osmotic Treatment

Some qualitative observations were recorded during the process. Treated carrot cubes from the contactor were found with a very bright reddish color. Shrinkage was observed in the treatments with 35% sucrose/22% NaCl after 65 minutes contact time. In the equilibrium study (to be discussed later), shrinkage was found by many observers. Le Maguer and Biswal (1984) observed that the shrinkage was complete within the first 30 minutes of contacting. Total shrinkage of carrot cubes was found to be 20% for NaCl-water solution. This suggests that for a ternary system of NaCl-sucrose-water, shrinkage cannot be ignored

without introducing an error in the mass transfer calculations, particularly for the equilibrium study.

The preliminary analysis for the osmosed samples showed that the hydrolysis of sucrose into glucose and fructose took place very quickly when osmosed samples were stored in the cold room at 4°C before HPLC analysis. The analysis procedure was therefore standardized by having all osmosed samples from the contactor or equilibrium study extracted immediately or only stored in the cold room for one night. This method has reduced the hydrolysis during the storage and variation in the analysis.

With automation in commercial processing , the osmosed samples will go to drying or freezing directly. If osmosed samples are used to produce intermediate moisture food or shelf stable food, the enzymes must be inactivated as soon as possible further to the osmotic treatment.

5.1.7 Summary of the General Performance of the Contactor

From the pilot-plant test of this continuous operation, it can be seen that the continuous process is one of the most efficient operations in terms of water loss. The optimum condition found was 44% sucrose /7% NaCl at 16 minutes contact. Substantial reduction of contact time to achieve the same results is a very promising aspect for application to commercial production. It also minimizes the unfavourable changes resulting from a process that requires long contact time. With some modifications, the potential applications of this process are very

substantial. For example, a belt dryer and a spraying water system could attach to the contactor to rinse the surface of the osmosed products before they go to the drying equipment. Most previous work was done using a small cube or thin pieces of fruit soaked in a large quantity of osmotic solution which could not be scaled up to a commercial production size operation. This study uses a continuous process on a pilot-plant osmotic contactor and undoubtedly provides useful information for a commercial operation.

Pilot-plant continuous study demonstrated the potential design and operational problems of a commercial osmotic process. One major problem was the spray system which easily became clogged with small pieces of material and viscous solutions. This study used very typical viscous, concentrated solutions, and therefore, the problem of external flow rate variation was noted in some experiments.

One limitation on large scale production, using an osmotic concentration process, is the quantity of osmotic solution left at the end of the process. In this study, the small quantity of carrot cubes in a large quantity of osmotic solution provided good condition for theoretical studies. However, in a real situation, the osmotic solution could be used for more than three runs. Further investigation should be done on the possibility of reusing the solution in order to make the process economically feasible.

5.2 Equilibrium Study

The objective of the equilibrium study is to determine the mass

transfer driving forces between the surface and inside materials. Parameters include mass loss (ML), water loss (WL), sugar gain (SUG) and sodium chloride gain (SCG) as well as the limiting composition of the carrot tissue in different sucrose/sodium chloride concentrations of osmotic media.

5.2.1 Experimental and Calculated Equilibrium Parameters of Carrot Tissue as a Function of Concentration of Osmotic Solution

The experimental measurement of total solids content (TS), sugar content (SUC), sodium chloride content (SCC) and density (ρ) are illustrated in table 5.6. Experiments A, B, C, D utilized the same concentration in the osmotic solution as the experimental runs on the osmotic contactor in order to determine the extent of osmotic dehydration. For these sets of experiments, the ratio of osmotic solution to carrot cubes were about 21:1. The other four experiments (E, F, G and H) were run at the ratio of approximately 8:1.

Data on total solids, sugar content, sodium chloride content and density was treated statistically using an Anova test followed by a Duncan Multiple Range Test (DMRT). Among the results to be noted is the fact that the percentage solids can be increased by a factor of three or more (average initial solids in carrot tissue was 11.8%) and this occurs with simultaneous loss of water and uptake of solids. From table 5.7, it also can be seen that there is no significant difference among the total solids in the carrot samples of the treatment A, B, C and D, but there is different between treatment A, B, C, D and E, F, G, H. This is

Table 5.6 Experimental Measurements of Density (ρ), Total Solids (TS), Sugar Content (SUC) and Sodium Chloride Content (SCC) of Carrot Cubes in Equilibrium with an Osmotic Solution at 45°C.

	Solution		Total Solids	Sugar Content	NaCl Content	Density (ρ)
	Sucrose(%)	NaCl(%)	(%)±SD	(%)±SD	(%)±SD	±SD
A	47	8	44.03±0.11	30.72±0.79	7.79±0.34	NA
B	44	7	42.14±0.66	29.32±0.35	6.31±0.76	NA
C	35	22	42.31±0.20	24.59±0.57	13.22±0.58	NA
D	30	18	42.59±0.19	22.63±0.54	10.21±0.57	NA
E	*41	2	36.90±0.16	27.22±0.09	1.17±0.31	1.13±0.01
F	*36	4	37.50±0.01	24.40±0.18	2.41±0.11	1.14±0.07
G	*33	8	38.20±0.02	23.14±0.56	4.28±0.17	1.17±0.01
H	*28	10	39.16±0.09	20.43±0.32	5.93±0.10	1.18±0.01

* Ratio of osmotic solution to carrot cubes was 8.3

DMRT

α = 0.05

TS: E F G H B C D A

SUC: H D G F C E B A

SCC: E F G H B A D C

because the concentration of total solids in the osmotic solution of the treatment A, B, C and D were around 50% to 55% (w/w), while the concentration of total solids in the solution of the treatment E, F, G and H was around 40%. This result dicates that the total solids of the osmotic solution also plays an important role in osmotic dehydration.

The sugar contents are not different between treatment H and D, and between D and F, but significant different from others. Sodium chloride content of the treatment H and B did not differ from each other. As mentioned previously, a high concentration of that species in the mixture of osmotic solution will result in a high gain of that species. Density for the treatments E, F, G and H were not significantly different from each other from a statistical point of view.

Based on the experimental measurements, the following equilibrium parameters have been calculated according to the method mentioned previously: mass loss (ML), water loss (WL), sugar gain (SUG), sodium chloride gain (SCG) and soluble solids loss (SSL).

These parameters are reported in table 5.7 for treatments A, B, C and D. From table 5.7, the mass loss appears to go through a minimum value of approximately 13.15% at 35% sucrose/22% NaCl solution. The highest mass loss (28.27%) was found with the treatment of 47% sucrose/8% NaCl. The water loss during an osmotic treatment varies from 37.15% to 45.96%. The maximum water loss was found with the treatment of 44% sucrose/7% Nacl. This is in agreement with Lenart and Flink (1984a) who stated that the osmotic mixture of 45% sucrose/5% Nacl or 40% sucrose/10% NaCl are the most effective osmotic concentrations in terms of water loss and weight reduction. The final amount of water

Table 5.7 Equilibrium Parameters: Mass Loss (ML), Water Loss (WL), Sugar Gain (SUG), Sodium Chloride Gain (SCG) and Soluble Solids Loss (SSL) of Carrot Cubes in Equilibrium with an Osmotic Solution at 45°C.

Solution		Mass Loss (ML)	Water Loss (WL)	Sugar Gain (SUG)	NaCl Gain (SCG)	Soluble Solids Loss
Sucrose (%)	NaCl (%)	(%)+SD	(%)+SD	(%)+SD	(%)+SD	(%)
A 47	8	28.27±0.59	45.92±2.01	14.65±0.57	5.40±0.96	2.40
B 44	7	27.14±2.08	45.96±1.39	13.74±0.89	4.35±0.23	0.73
C 35	22	13.15±4.00	37.35±1.56	13.55±0.63	11.10±0.41	0.45
D 30	18	25.16±1.23	43.59±1.01	9.89±0.30	7.60±0.36	0.94

loss was similar to those observed by Flink (1980) for equilibrium study. Sugar gain was steadily increased with the increased concentration of osmotic solution. An analysis of salt gain in carrot tissue indicates that the percentage of the salt gain is proportional to the percentage of salt in the osmotic solution.

The maximum water loss and mass loss were found with the treatments in 47% sucrose/8% NaCl and 44% sucrose/7% NaCl. This is in agreement with the optimum condition found in the operation of the contactor.

5.2.2 Comparison

The values of M/M_o, M_w/M_o, M_{su}/M_o and M_{sc}/M_o at the operation 55 minutes contact and equilibrium conditions is listed in table 5.8. It is interesting to note that the values of M/M_o are higher when in the equilibrium than that in the operation with 55 minutes contact time, indicating that mass loss was less in the equilibrium than in the operation. The substantial uptake of solutes in the equilibrium situation contributes to the lower mass loss. M_w/M_o is less when in equilibrium than in the 55 minute operation except with the 35% sucrose / 22% NaCl run. Both the increase in sugar and NaCl gain indicate that the result is far away from equilibrium.

These results provide important process parameters using a short contact time. Water reduction is substantial without much sugar and salt uptake.

5.3 Fluxes

Table 5.8 Comparison of M/Mo, Mw/Mo, Msu/Mo and Msc/Mo at Equilibrium (24 hr) and Operation (55 min) Condition

	Solution					
	Sucrose (%)	NaCl (%)	$\frac{M}{Mo}$	$\frac{Mw}{Mo}$	$\frac{Msu}{Mo}$	$\frac{Msc}{Mo}$
	30	18	0.75	0.43	0.17	0.08
	44	7	0.75	0.43	0.22	0.04
I	47	8	0.72	0.40	0.22	0.06
	35	22	0.87	0.50	0.21	0.11
	30	18	NA	NA	NA	NA
	44	7	0.70	0.55	0.12	0.01
II	47	8	0.70	0.50	0.13	0.02
	35	22	0.63	0.41	0.11	0.07

Note: I — Equilibrium condition (contact time 24 hr)

II — Operation condition (contact time 55 min)

5.3.1 Experimental Flux as a Function of Time

With reference to Eq. [3.33]:

$$J_i = - \frac{a\rho_c}{6 \frac{M}{M_o}} \left[\frac{d(M_i/M_o)}{dt} \right]$$

Assuming a and ρ_c remain constant throughout the process, ρ_c = 1064 kg/m^3, a = 0.0085 m; M/M_o is the mass ratio of carrot cubes at time t over initial mass M_o. M_i/M_o is the mass of species i at time t over initial mass (M_o).

The diffusional flux of component i was calculated according to M/M_o and M_i/M_o fitted curves and derivatives through Eq. [5.14] to [5.19]. For simplicity purposes, J_w, J_{su}, and J_{sc} have been reduced to their dimensionless forms as shown below.

$$J'_w = J_w / J_{w,max}$$

$$J'_{su} = J_{su} / J_{su,max}$$

$$J'_{sc} = J_{sc} / J_{sc,max}$$

where $J_{w,max}$, $J_{su,max}$ and $J_{sc,max}$ are the values at time zero, and J'_w, J'_{su} and J'_{sc} are reduced fluxes of water, sucrose and sodium chloride, respectively. These dimensionless fluxes under different operational

conditions as a function of time are shown in Fig. 5.7, Fig. 5.8 and Fig. 5.9. The nonlinear exponential functions were observed for all the fluxes. As time increases, all the fluxes approach zero. This indicates the reality of the osmotic process.

5.3.2 General Equations for Prediction of Fluxes

As mentioned in Chapter 3., the calculated fluxes were related to the driving forces through phenomenological equations. The independent variables were the chemical potential difference of water over temperature ($X_1 = \Delta\mu_w/T$), the chemical potential difference of sucrose over temperature ($X_2 = \Delta\mu_{su}/T$) and the chemical potential difference of NaCl over temperature ($X_3 = \Delta\mu_{sc}/T$). The responses chosen as dependent variables were the fluxes of water (J_w), sucrose (J_{sc}) and the NaCl (J_{sc}).

As illustrated in Eq. [3.14], Eq. [3.15] and Eq. [3.16], the square terms for every independent variable were considered. However, an attempt has been made to eliminate these square terms in the original model, thus the general flux is expressed as:

$$J_i = a_{i1} X_1 + a_{i2} X_2 + a_{i3} X_3 + a'_{12} X_1 X_2 + a'_{13} X_1 X_3 + a'_{23} X_2 X_3 \qquad [5.20]$$

Where a_{ij}, a'_{ij} and a''_{ij} are phenomenological coefficients, an analysis through multi-linear repression (SPSS-X, 1985) was applied to

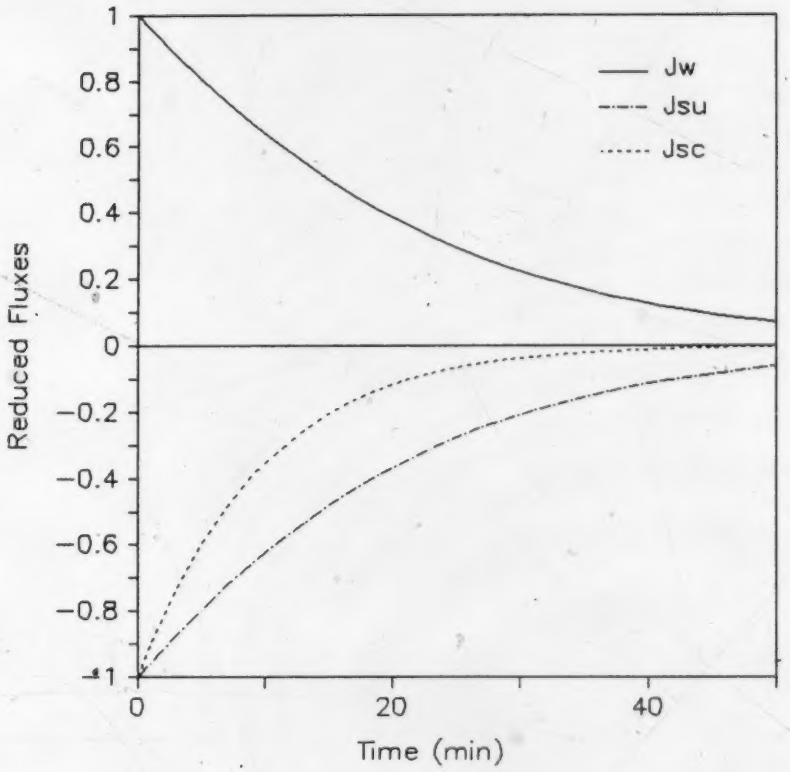

Fig. 5.7 The Reduced Fluxes of Water(Jw), Sucrose (Jsu) and Sodium Chloride (Jsc) as a Function of Time at 44% Sucrose/7% NaCl Solution

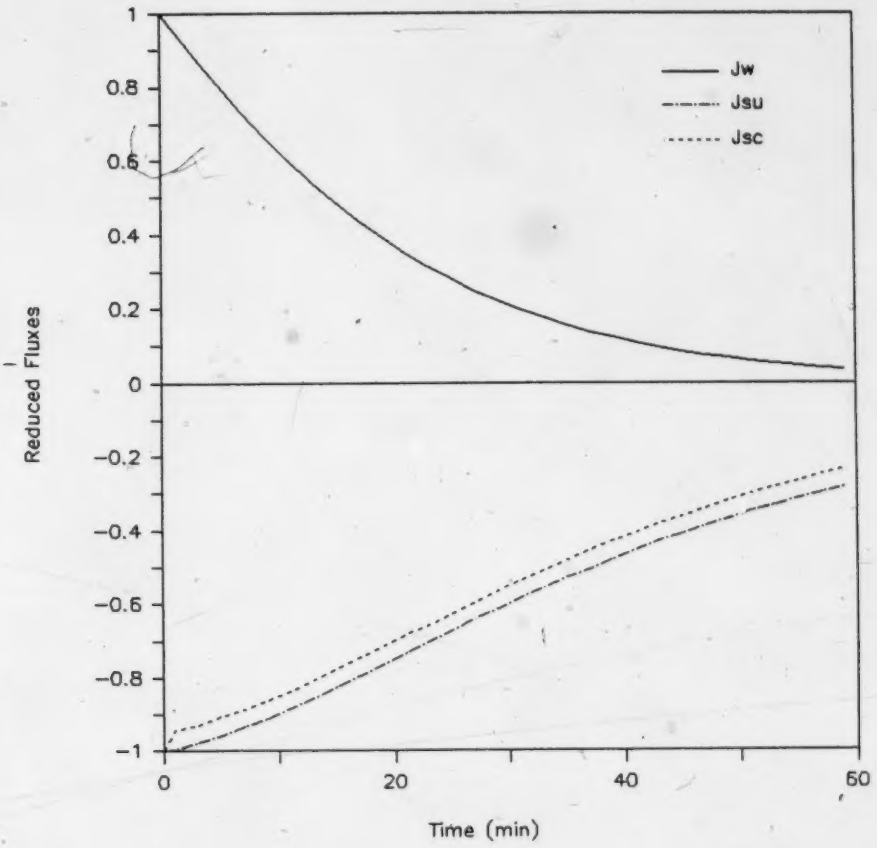

Fig. 5.8 The Reduced Fluxes of Water (Jw), Sucrose (Jsu) and Sodium Chloride (Jsc) as a Function of Time at 47% Sucrose/8% NaCl Solution

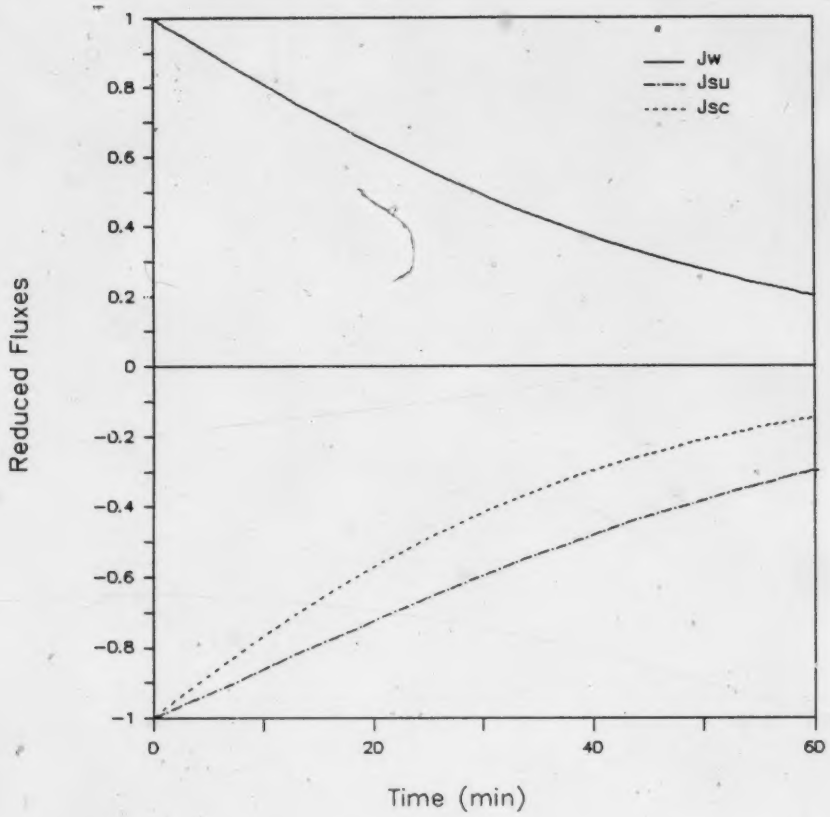

Fig. 5.9 The Reduced Fluxes of Water (Jw), Sucrose (Jsu) and Sodium Chloride (Jsc) as a Function of Time at 35% Sucrose/22% NaCl Solution

estimate the coeffients, respectively. The estimated coeffients are listed in Table 5.9. Satisfactory results of correlation coefficients (R^2 = 0.9825 for J_w, R^2 = 0.9653 for J_{su} and 0.9831 for J_{sc}) were obtained only with these six terms, X_1, X_2, X_3 and interactions between them. By further observation, it was also noted that, X_1, X_2, X_3 are more significant to the fluxes than the interaction terms. For simplicity, it was decided that these emprical equations would be used for the prediction of fluxes of water, sucrose and NaCl at all the conditions throughout the continuous osmotic process.

The predicted fluxes were reduced to dimensionless values by dividing each by their initial value. These predicted reduced fluxes were compared with calculated reduced values from curve fitting with the experimental data, and typical curves are shown in Fig.5.10, Fig.5.11 and Fig.5.12. As shown in Fig.5.10, the water flux in 47% sucrose / 8% NaCl was in good agreement between calculated and predicted values and with %RMSD=1.0% (%RMSD refers to % root mean square of deviation). Good results were also obtained for salt flux between calculated and predicted values with %RMSD= 7% (Fig. 5.12). However, it can be seen in Fig.5.11, there was an overestimation in the first 30 minutes and underestimation between 35 to 50 minutes for sucrose flux with large error of 20%. This discrepancy may be because shrinkage was not taken into consideration in the calculation of flux, but it was taken into account in the prediction. It is also suspected that the permeability of living cells makes the difference. Sucrose being considered an impermeable solute and can only penetrate into the extracellular volume of the cell. However, in the evaluation of the chemical potential of

Table 5.9 Transport Coefficients as Obtained Through Multi-linear Regression for the Prediction of Fluxes

Forces	J_w	J_{su}	J_{sc}
X_1	3.197×10^{-6}	-1.093×10^{-6}	-1.036×10^{-7}
X_2	2.549×10^{-5}	7.727×10^{-7}	-6.394×10^{-7}
X_3	-7.298×10^{-7}	-2.813×10^{-7}	-4.383×10^{-8}
X_1X_2	-4.357×10^{-7}	-1.266×10^{-8}	1.861×10^{-8}
X_1X_3	2.000×10^{-8}	-1.047×10^{-9}	7.257×10^{-10}
X_2X_3	1.858×10^{-8}	-3.520×10^{-9}	-9.457×10^{-11}
R^2	0.9825	0.9653	0.9831

Note:

$$X_1 = \frac{\Delta\mu_w}{T}$$

$$X_2 = \frac{\Delta\mu_{su}}{T}$$

$$X_3 = \frac{\Delta\mu_{sc}}{T}$$

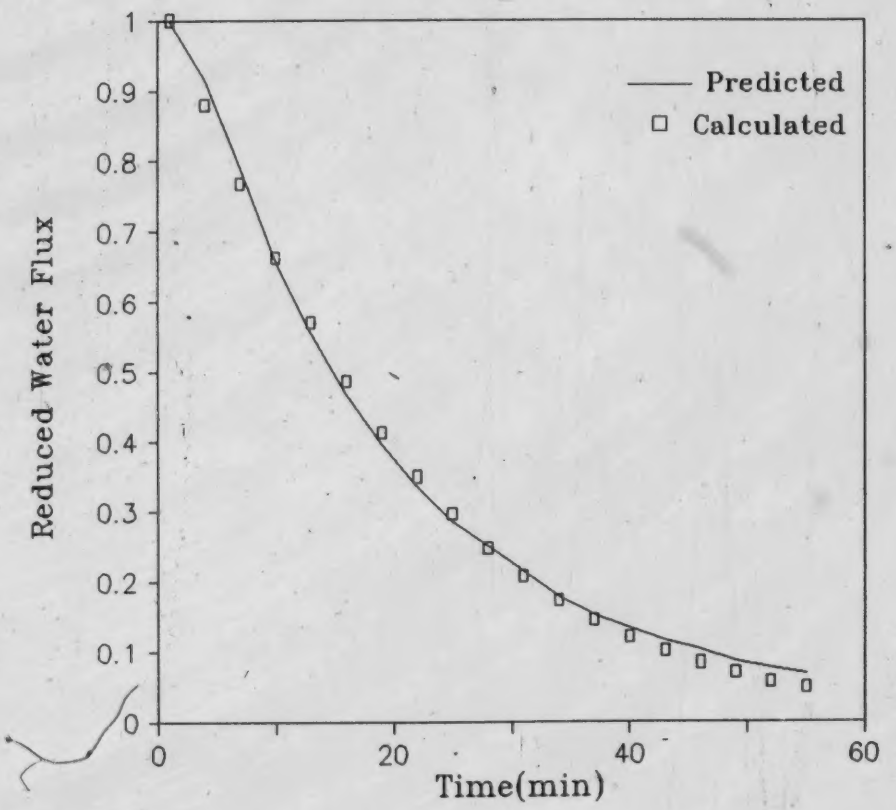

Fig. 5.10 Calculated and Predicted Values of Reduced Water Flux for a Typical Run (47% Sucrose/8% NaCl)

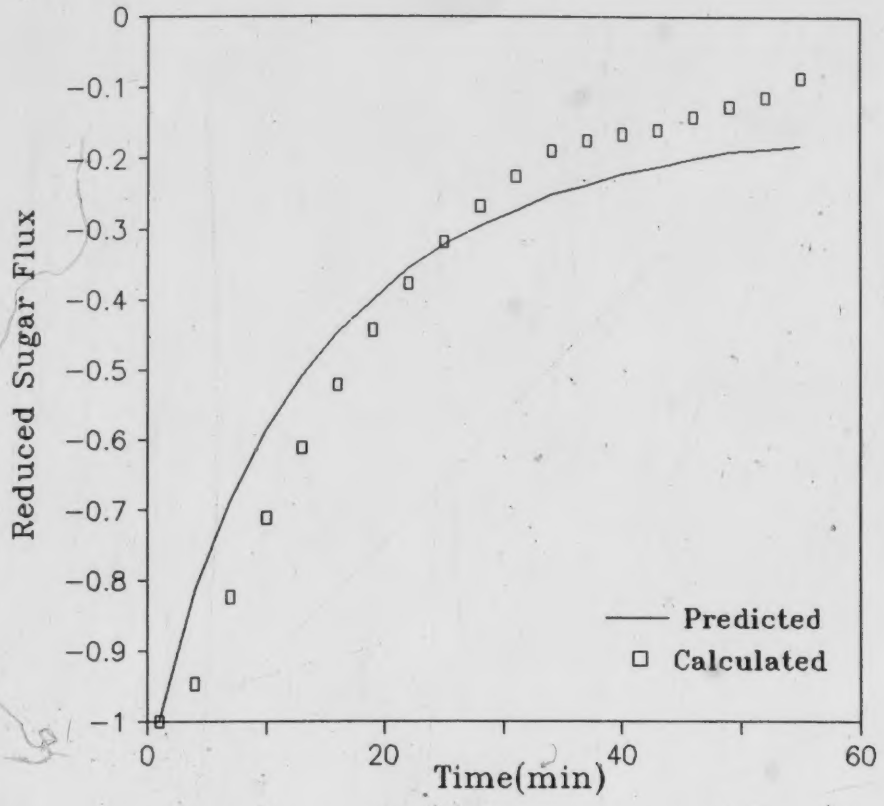

Fig. 5.11 Calculated and Predicted Values of Reduced Sucrose Flux for a Typical Run (44% Sucrose/7% NaCl)

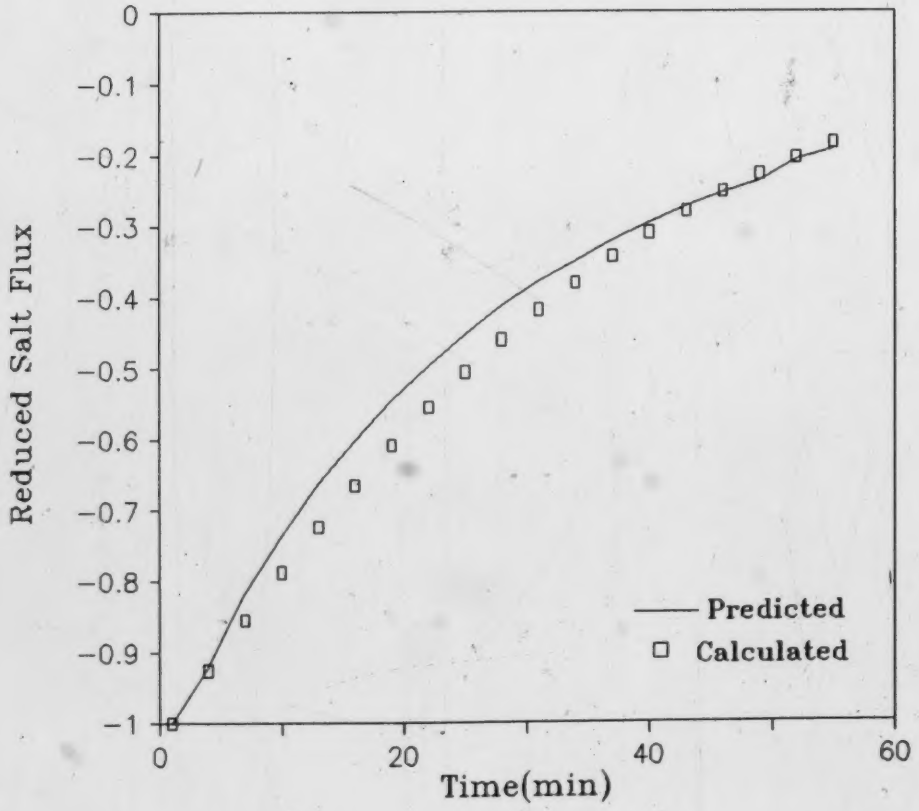

Fig. 5.12 Calculated and Predicted Values of Reduced Sodium Chloride Flux for a Typical Run (35% Sucrose/22% NaCl)

sucrose, the average concentration of sucrose was used on a total cellular volume basis. This calculation reduced the average concentration inside the cell because only the extracellular volume is occupied by the osmotic solution. Thus, the chemical potential difference (X_2) was increased. Incorrect estimation of X_2 may have contributed to the error involved in the flux estimation. By examining the coefficients of X_2 in table 5.9, the chemical potential of sucrose appears to be a dominant variable in mass transport which reveals the important role of the living cell and impermeable solutes in the osmotic process. Nevertheless, the predicted results obtained in this study are accurate enough for practical use.

5.4 Validation of the Model

5.4.1 Description of the Numerical Methods and Testing the Step

There are many numerical methods available to solve differential equations. However, the most widely used methods of integration for ordinary differential equations where only initial values are known are Runge-Kutta methods. They are very suitable for solving initial-value problems because they are self-starting from a given initial point of integration. Furthermore, they are very efficient and a larger step could be used with the same accuracy compared to the other method. In a general form, the integration formula for the differential equation is given as:

$$y_{i+1} = y_i + \sum_{j=1}^{m} W_j k_j \qquad [5.21]$$

$$k_j = h\, f(x_i + c_j h,\ y_i + \sum_{i=1}^{j-1} a_{jl} k_j \qquad [5.22]$$

The Fourth-order Runge-Kutta is the most widely used numerical integration method. The local error involved in Fourth-order Runge-kutta $0(h^5)$ and the global was $0(h^4)$.
The formula is:

$$y_{i+1} = y_i + 1/6\ (k_1 + 2k_2 + 2k_3 + k_4) \qquad [5.23]$$

$$k_1 = h\, f\ (x_i,\ y_i) \qquad [5.24]$$

$$k_2 = h\, f\ (x_i + h/2,\ y_i + k_1/2) \qquad [5.25]$$

$$k_3 = h\, f\ (x_i + h/2,\ y_i + k_2/2) \qquad [5.26]$$

$$k_4 = h\, f\ (x_i + h,\ y_i + k_3) \qquad [5.27]$$

In applying this method, one always uses the previous k-value in incrementing the function values and the value of h to increment the independent variable. Fouth-order Runge-Kutta was chosen and used to evaluate the weight fraction change along the contactor (a function of contact time). The models were easily solved since the initial composition of carrots was known.

Three different incremental steps of 60, 30, and 15 seconds were tested. Convergence was rapid. It was found that the maximum relative error between 60s and 30s was 0.15% and 0.08% between 30s and 15s. They are very small values compared with the experimental error. Therefore, an increment step of 15 seconds was chosen for the program.

5.4.2 Comparison between the Predicted and Experimental Values of Sucrose, NaCl and Water Content

The validity of the model was tested with the predicted weight fractions of water, sucrose and NaCl content compared with those of experimental values over the contact time range of 16 to 60 min. The results are shown in Fig. 5.13 for the weight fraction of water. It can be seen that an excellent prediction value for the weight fraction of water was obtained with an average %RMSD of 1.0%. As Fig. 5.14 illustrates, the prediction for the weight fraction of sucrose is good with an average error of less than 5%. And the prediction for the weight fraction of sodium chloride was found to be acceptable with %RMSD=10.7% (Fig. 5.15). It is not surprising to find this predicted error due to a direct result of experimental measurements. Errors from the prediction of activity coefficients are also to be expected. Lee (1987) pointed out that the solute activity coefficients in the ternary sucrose/sodium chloride water system were correlated accurately with the extended UNIQUAC equation. The average %RMSD of the salt and sucrose activity coefficients were 8% to 5% respectively. Therefore we may conclude that the model is good enough for practical use within the

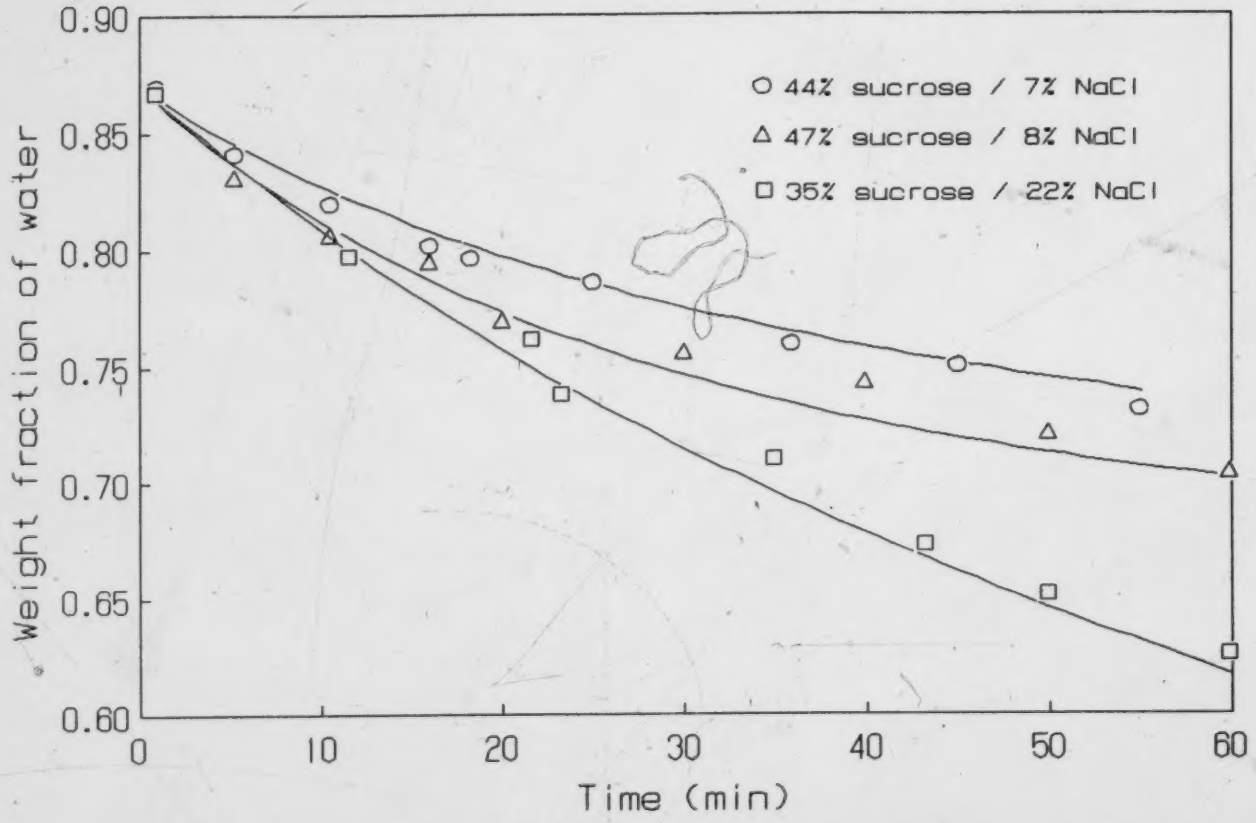

Fig. 5.13 Experimental and Predicted Weight Fraction of Water at Different Conditions

(lines indicate predicted and dots are experimental)

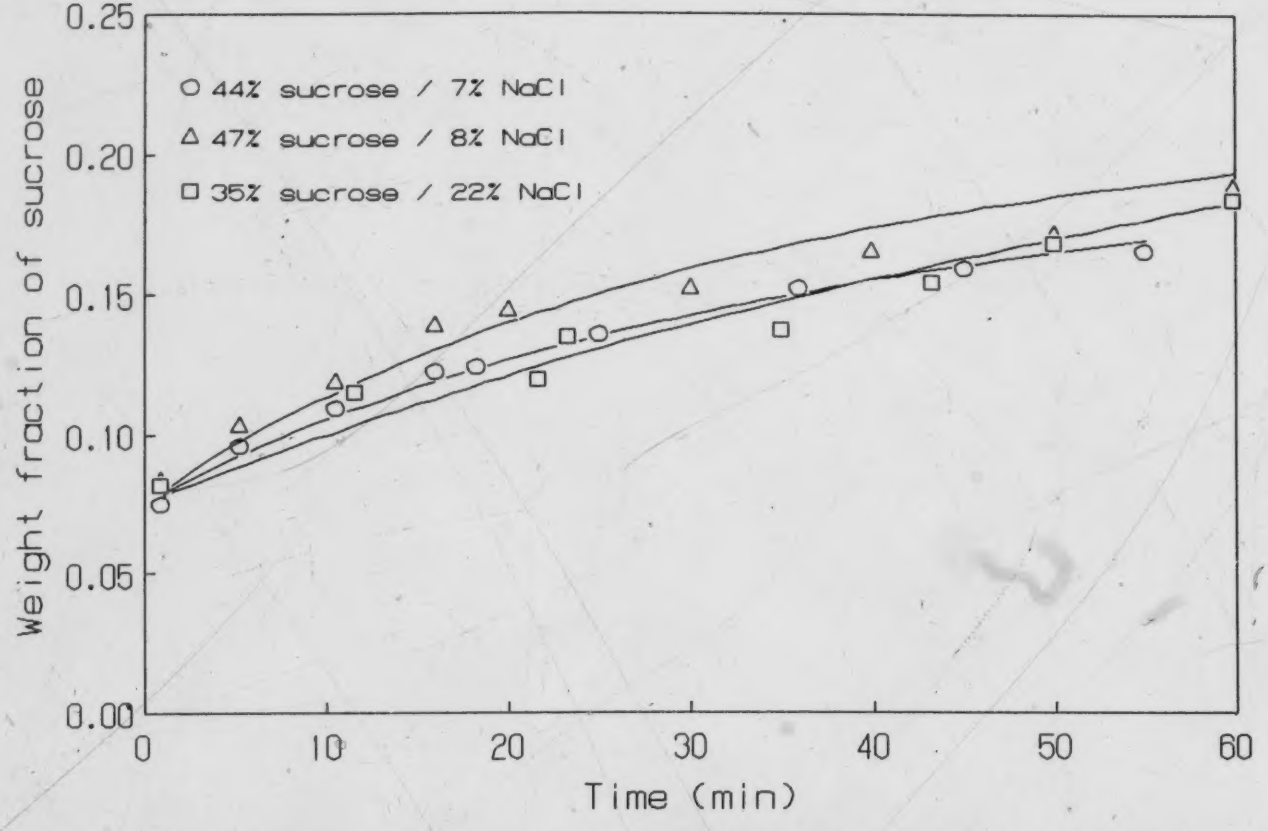

Fig. 5.14 Experimental and Predicted Weight Fraction of Sucrose at Different Conditions

(lines indicate predicted and dots are experimental)

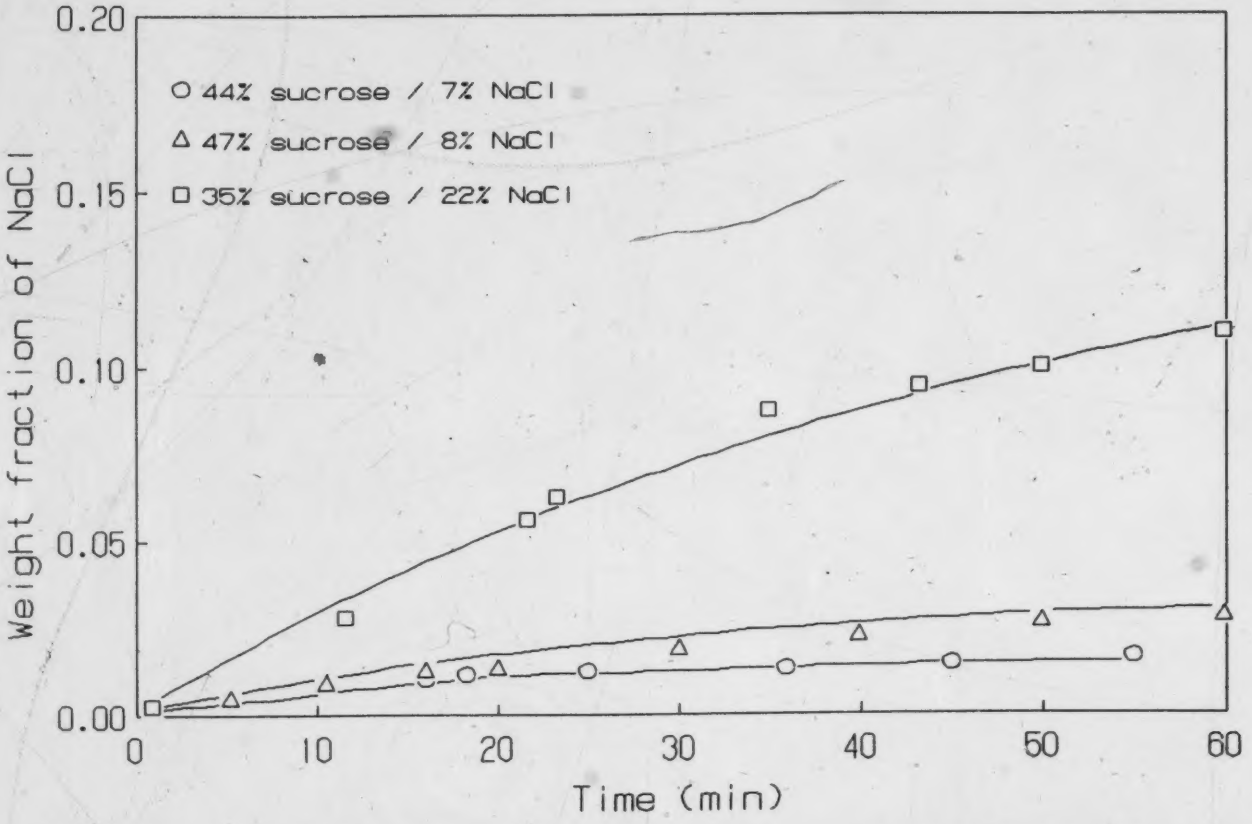

Fig. 5.15 Experimental and Predicted Weight Fraction of NaCl at Different Conditions

(lines indicate predicted and dots are experimental)

experimental region.

5.5 Model Prediction

5.5.1 Parametric Studies

The role of specific parameters in the overall osmotic behavior of carrot tissue can be illustrated quite effectively by taking advantage of the predictive characteristics of the model to generate the response of the studied system and by varying the magnitude of these parameters.

Three major properties will be examined in the following analysis: water loss (WL), or the ratio of water loss to solid gain, the ratio of salt to sugar in the osmotic solution (R), and contact time (t). It should be mentioned that total solids (NaCl+sucrose) in the osmotic solution were kept to 55% (W/W) in this analysis. The three dimensional graphical approach was adopted to illustrate the response as two factors vary simultaneously. In this approach, predictive models were used to create contour surfaces or contour lines within the experimental region. The contour surfaces and contour plots were created on three and two coordinate diagrams, respectively. Theoretically, these surfaces and plots present accurately the trend within the experimental region.

The typical response surface of water loss and the corresponding contour plot as a function of contact time and the ratio of salt to sugar in the solution (R) is illustrated in Fig.5.16 and Fig.5.17. It can be seen that water loss increases with the increase of the contact time and R value. However, there is an optimum condition around 56

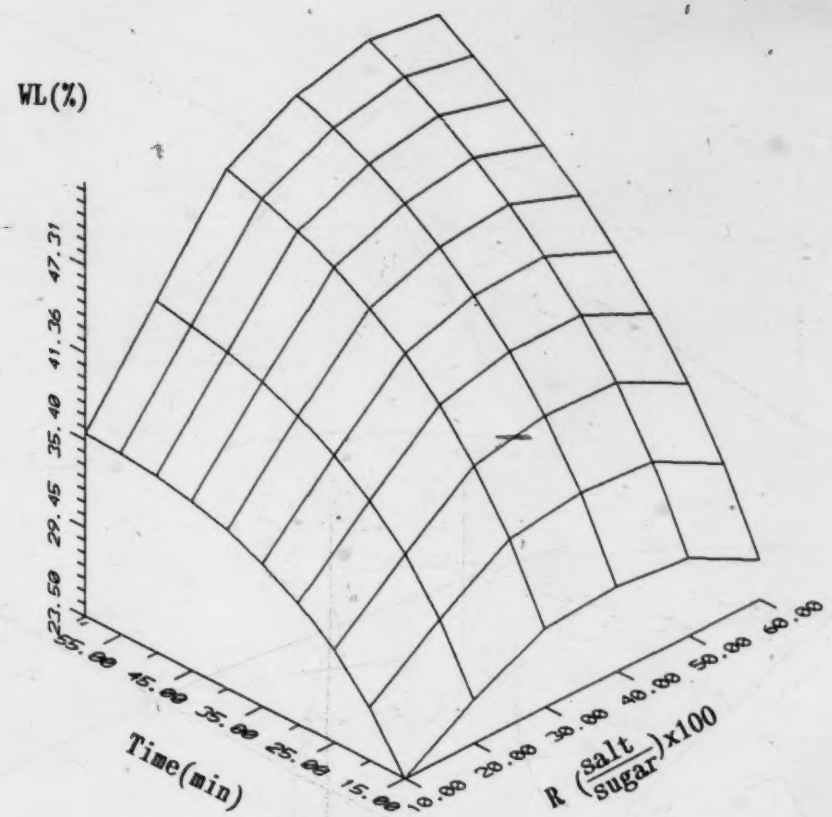

Fig. 5.16 Response Surface of Water Loss as a Function of Time and the Ratio of Salt to Sugar in the Osmotic Solution

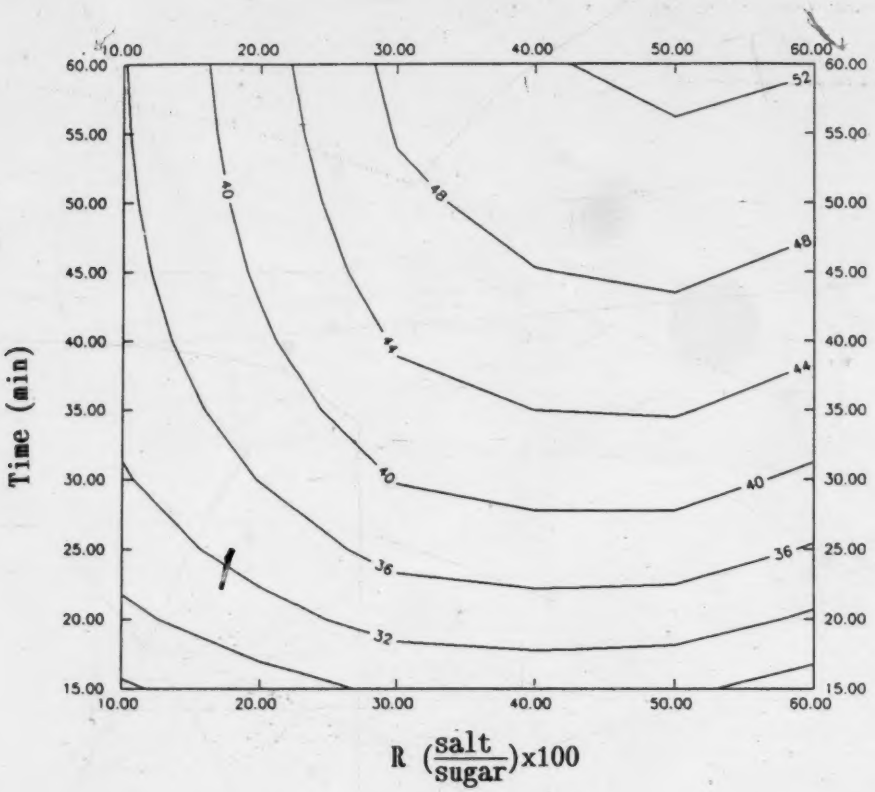

Fig. 5.17 The Contour Plot of Water Loss as a Function of Time and R

minutes contact time when *R* is about 0.5 which resulted in 54% water loss (Fig. 5.17). It is interesting to notice that from 44% water loss or less, for a given contact time, there is a range of *R* value corresponding to that response. For example, if we keep contact time around 15 minutes, the *R* value varies from 0.3 to 0.5 to get same percentage of water loss (around 28). Therefore the smallest *R* value (indicating less salt) is considered as an optimum condition for that response.

In order to evaluate the overall changes in the osmotic mass transfer process, the water loss over solid gain (sugar+salt) in the carrot tissue was considered as a response and shown in Fig.5.18. The ratio of water loss over solid gain contour as a function of contact time and the ratio of salt to sugar in the osmotic solution (*R*) was presented in Fig.5.19. As we expected, the highest value was found with very short contact time. This in turn demonstrates that the osmotic process is a dynamic one which removes water rapidly in a short period of time with very little solid gain.

In general for an increase in the *R* value (increased salt in the osmotic solution) at a given contact time, the ratio of water loss over solid gain will increase due to the effect of salt on the water removal. If the *R* value is kept constant, the ratio of water loss over solids gain is substantially reduced due to the solids uptake when contact time is increased.

It is difficult to determine where the optimum conditions are. Although the ratio of water loss over solids gain is at maximum in the beginning, it will be important for industry to remove a certain

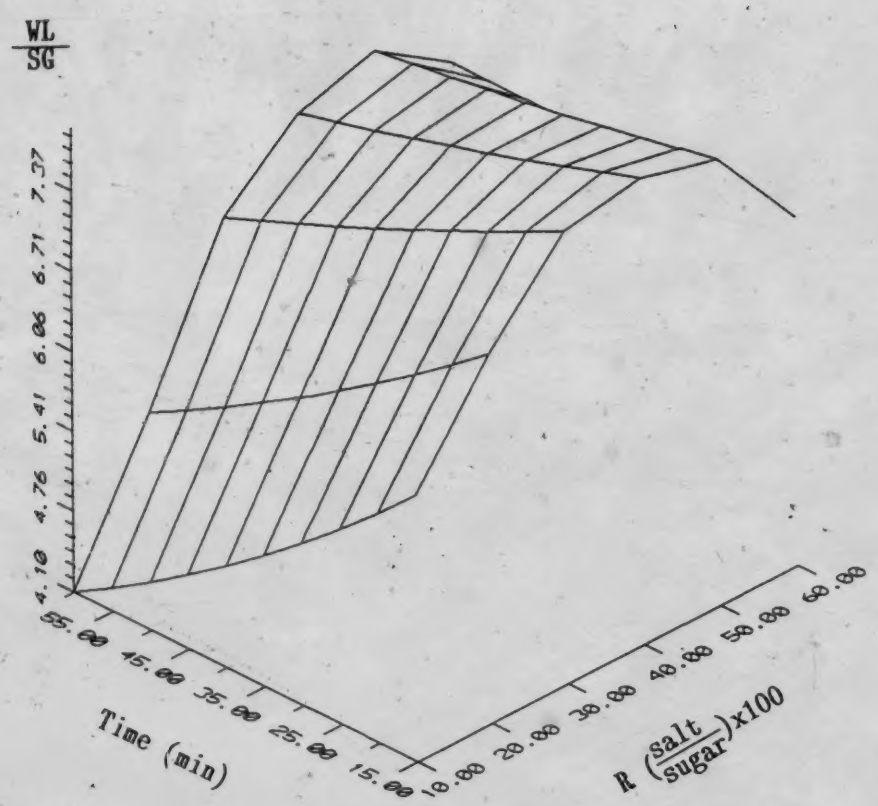

Fig. 5.18 The Response Surface of Water Loss to Solids Gain as a Function of Time and R

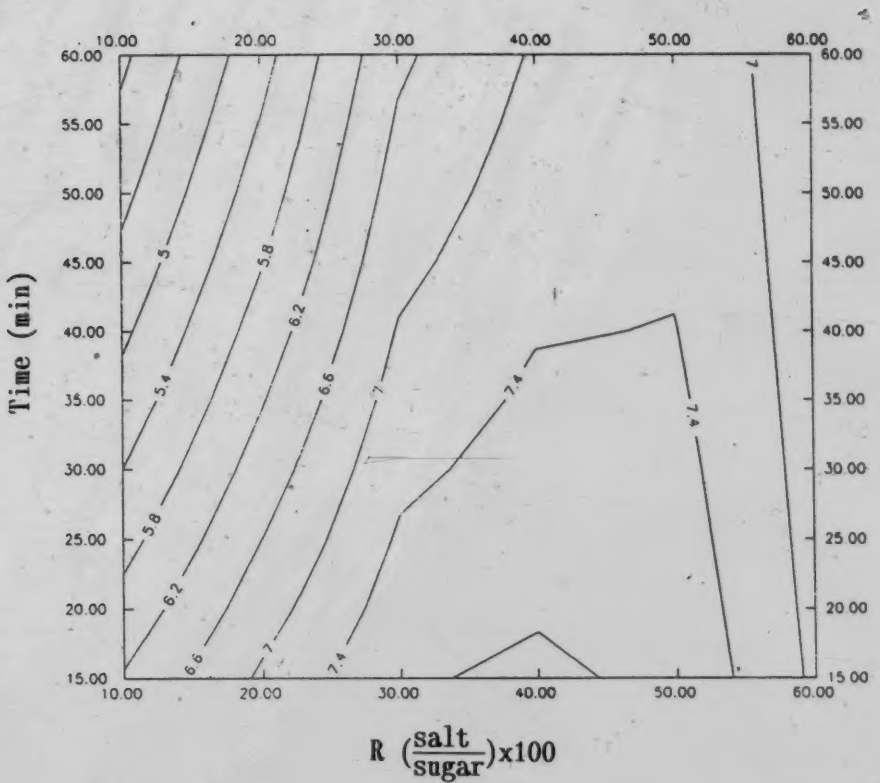

Fig. 5.19 Contour Plot of Water Loss to Solids Gain as a Function of Time and R

percentage of water over a period of time while trying to keep the ratio of water loss over solids gain as high as possible. From Fig.5.17, it can be seen that the minimum contact time to obtain a 30% water loss is about 17 minutes at R=0.35 which will be practical for commercial operation condition. From Fig. 5.19, at R = 0.35 with a contact time 17 minutes the ratio of water loss over solids gain is about 7.8. Therefore, amount of solids uptake is expected. Furthermore, the salt concentration in the final product is always considered as a criteria for the osmotic process. The response surfaces and contour plots provide us with very useful information for process parameter design and the relationship between the variables.

5.5.2 Simulation with a Sequence of Osmotic Solutions

It is of interest to evaluate the osmotic behavior of plant materials in contacting with different concentrations or compositions of osmotic solutions in varying sequences. Since this unit was arbitrarily divided into three sections, an attempt was made to alter the individual concentration of aqueous sucrose/NaCl solution circulated in its own section. The total solids in the solutions were kept at 55% (w/w).

As shown in Table 5.10, three different sequences were studied. Treatment A started with a 40% sucrose/15% NaCl in section I, with a proportional increase in sucrose concentration (with corresponding decrease in salt) in section II, Section III had a concentration of 50% sucrose/5% NaCl. Treatment B is the reverse of A, that is, it starts with 50% sucrose/5% NaCl in section I, then has a decrease in sucrose

Table 5.10 The Sequence of Osmotic Solutions

Treatment	Section I (Beginning)		Section II (Middle)		Section III (End)
A	40% sucrose	→	45% sucrose	→	50% sucrose
	15% NaCl		10% NaCl		5% NaCL
B	50% sucrose	→	45% sucrose	→	40% sucrose
	5% NaCl		10% NaCl		15% NaCl
C	45% sucrose	→	45% sucrose	→	45% sucrose
	10% NaCl		10% NaCl		10% NaCl

concentration, and an increase in NaCl in section II. It ends up with 40% sucrose/15% NaCl in section III. Treatment C maintained a concentration of 45% sucrose/10% NaCl from section I through section III.

Fig. 5.20 to Fig. 5.22 illustrated the course of water loss, sugar gain and salt gain in the carrot tissue as a function of time exposure to alternated osmotic media in the mentioned sequences with a contact time of 5 minutes in each section. As can be seen in Fig. 5.20, treatment A and treatment C have almost the same effect on water loss in section I and section II (before 10 minutes). However, the A line was suddenly flattened in section III.

Sugar gain was increased in sections I and II for A, B and C , while the slope of line B was decreased, but increased with A in section III (Fig. 5.21). Treatment A gave the highest salt gain in all the sections (Fig. 5.22) as well. Varying osmotic behavior, which resulted from different sequences of contacting together with different concentrations of sucrose/salt mixture, could be observed better if we increased the contact time in each section from 5 minutes to 14 minutes. As shown in Fig. 5.23, there was an increase in water loss in section I and II, but a dramatic decrease during treatment A in section III. This indicates that water started to return gradually into the tissue in order to maintain osmotic equilibrium. Treatment B exhibits an almost linear water loss and there was a big gap between treatment A and B in the first two sections.

Sugar gain increase was observed in section III with treatment A (see Fig. 5.24). In addition to the carrots being exposed to a highly

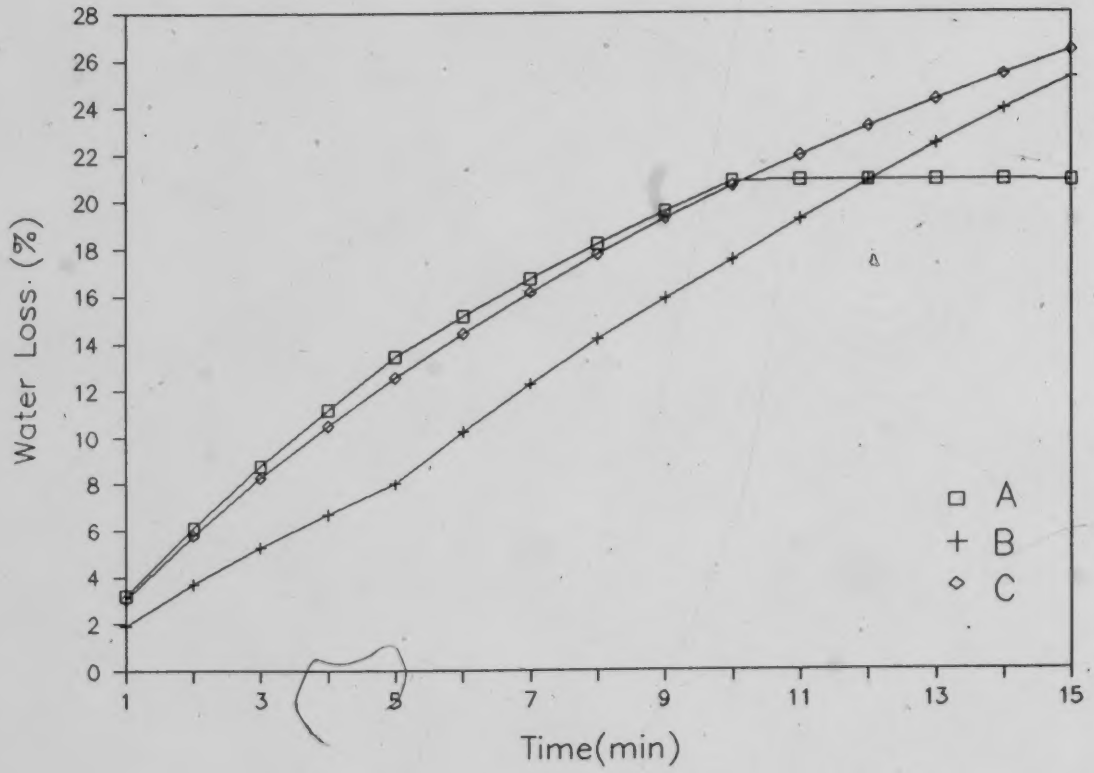

Fig. 5.20 Water Loss as a Function of Time with Different Concentration of Sucrose/NaCl Solution in Each Section
(contact time 5 min in each section)

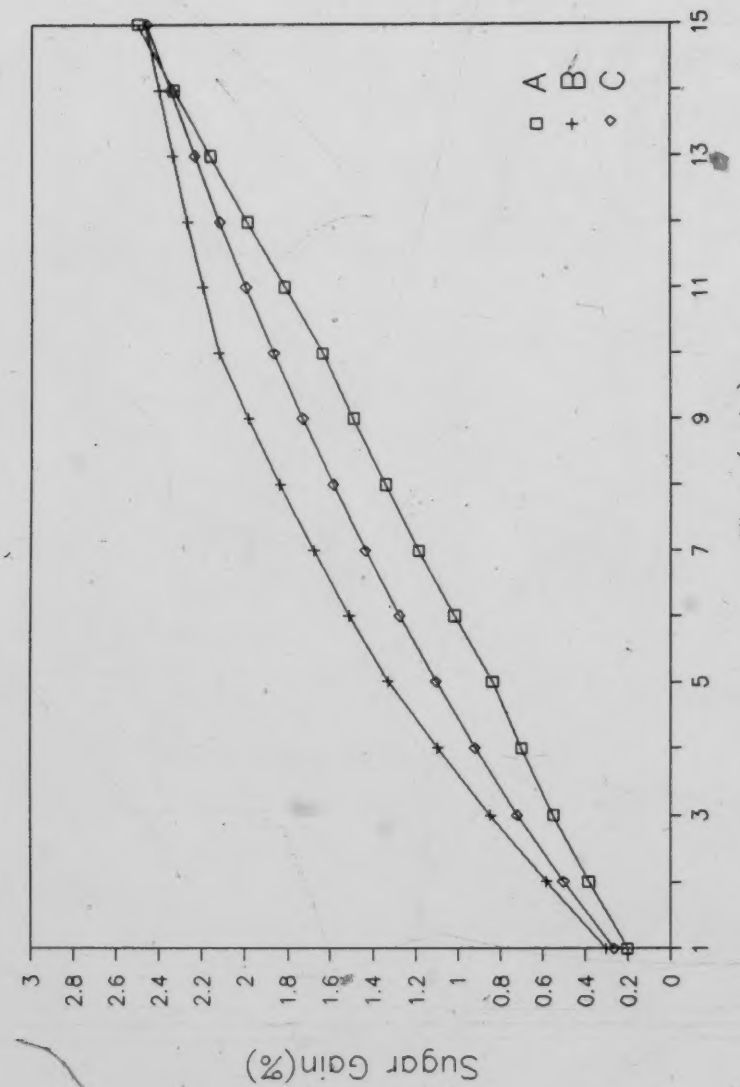

Fig. 5.21 Sugar Gain as a Function of Time with Different Concentration of Sucrose/NaCl Solution in Each Section
(contact time 5 min each section)

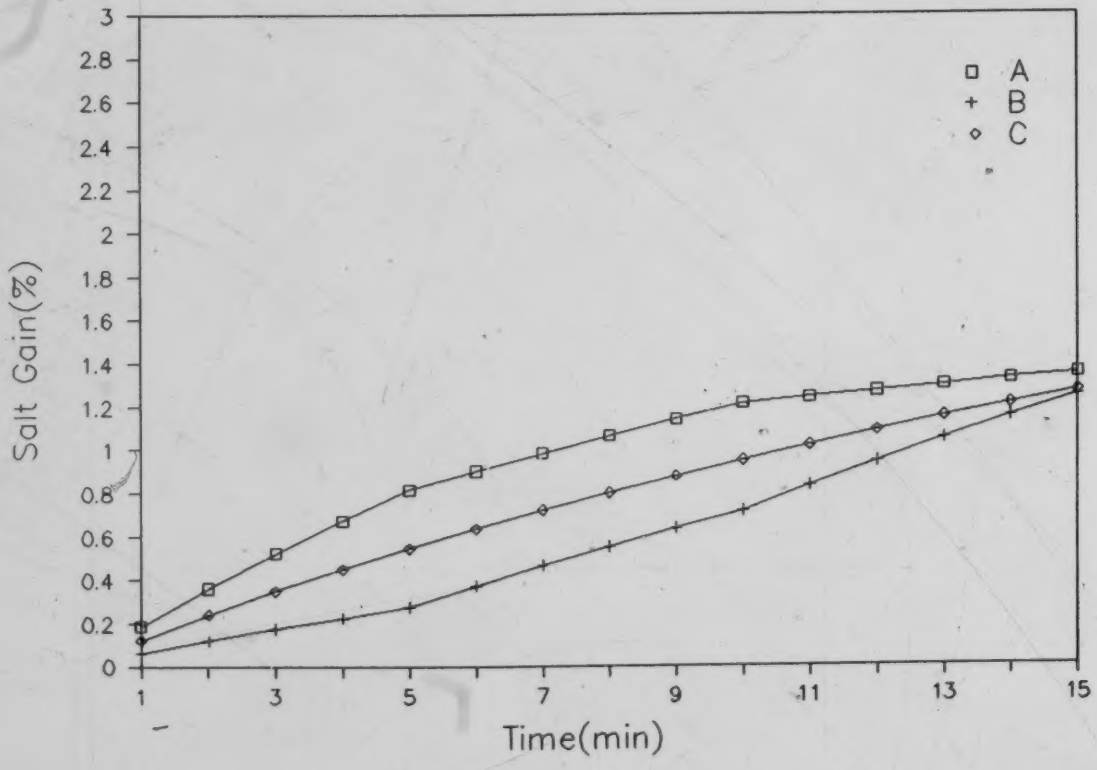

Fig. 5.22 Salt Gain as a Function of Time with Different Concentration of Sucrose/NaCl Solution in Each Section
(contact time 5 min in each section)

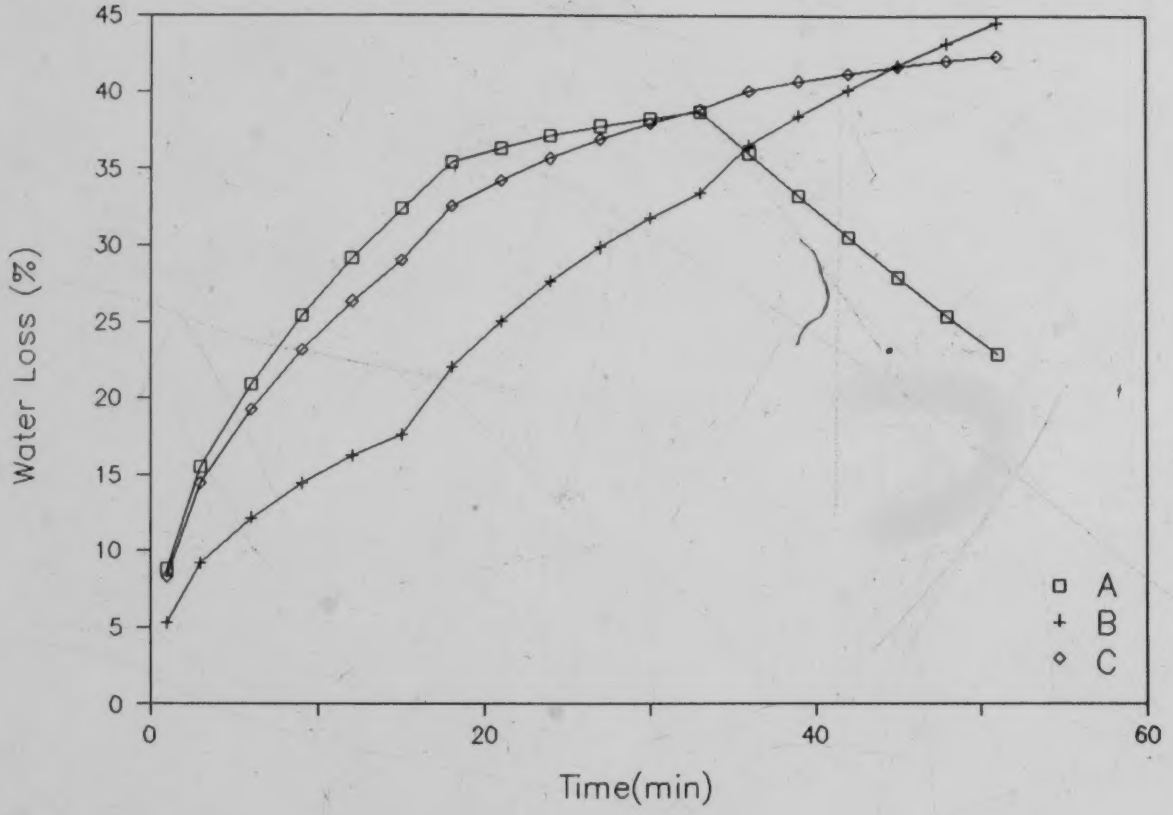

Fig. 5.23 Water Loss as a Function of Time with Different Concentration of Sucrose/NaCl Solution in Each Section
(contact time 14 minutes each section)

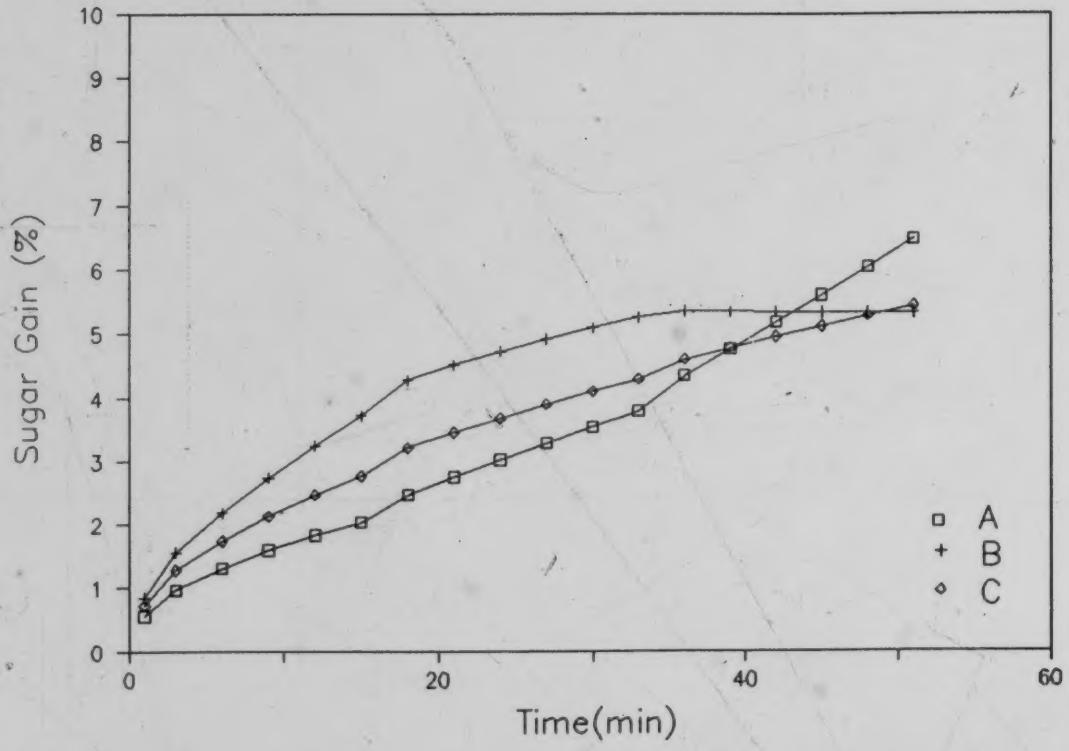

Fig. 5.24 Sugar Gain as a Function of Time with Different Concentration of Sucrose/NaCl Solution in Each Section
(contact time 14 minutes each section)

concentrated sucrose solution in this section, they may be influenced by the uptake of sodium chloride in the previous process. The softness of NaCl treated carrot cubes was found (Biswal and Le Maguer, 1987; Sterling, 1968).

As Sterling (1968) explained, the softness of NaCl treated carrots can be attributed to the lytropic effect of NaCl in the tissue. This lytropic effect is referred to the dispersion of polysacchride mole cubes by breaking hydrogen bonds. The effect of NaCl on the further weakening of carrot tissue is also due to the small amount of calcium/sodium ion exchange. As calcium is removed from the cell, Ca-pectate complexes of the middle lamella are destroyed, decreasing the cohesiveness of the cell and resulting in the softening of the tissue. We may assume that the permeability of the cell membrane was modified by the penetration of NaCl.

Resistance to the penetration of NaCl in the treatment B (section III, Fig.5.25) is due to the high concentration in sucrose which probably form a compact layer at the surface of the carrots which hindered the penetration of NaCl in the following sections. This response of the carrot tissue illustrated the difference in the osmotic effect of permeable and impermeable solutes and membrane properties. The simulation results revealed that alternating the different concentrations of sucrose/NaCl mixtures was not as successful compared to no alternation. This was especially true when starting with a high salt concentration mixture. The latter resulted in an unexpected decrease in WL and an increase in sugar gain in section III. A high salt gain due to the penetration of salt at the beginning and subsequent

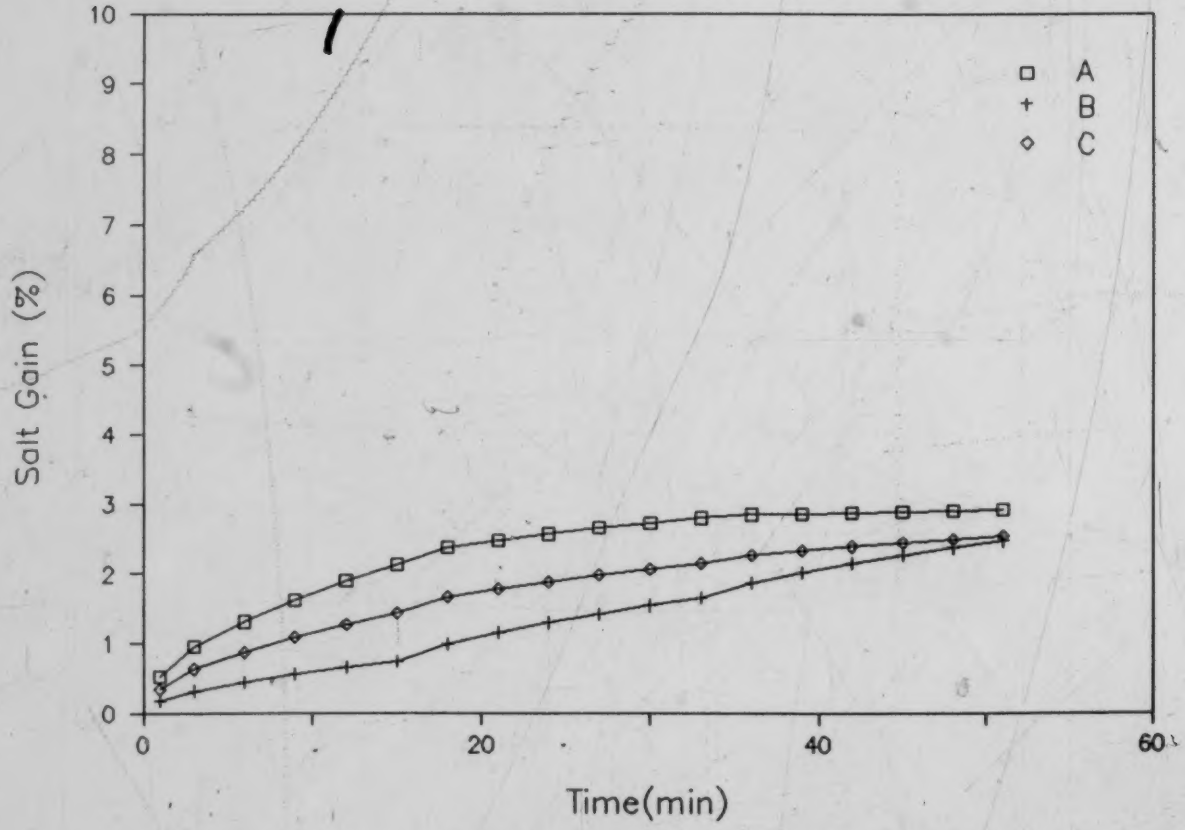

Fig. 5.25 Salt Gain as a Function of Time with Different Concentration of Sucrose/NaCl Solution in Each Section
(contact time 14 minutes section)

modification of the tissue composition induced a decrease in the driving force for the process which followed. With an increased contact time, there is a tendency to increase water loss in treatment B which began with a high concentration of sucrose in the osmotic medium. The results correspond with the literature. Hawkes and Flink (1980) also reported that osmosis in salt solutions, followed by sucrose solutions did not result in good dehydration potential. Verification of this phenomena could be tested on the contactor.

6 CONCLUSION AND RECOMMENDATIONS

In this study, a pilot-scale belt contactor was designed and demonstrated that a continuous cross-current coupled with a counter-current osmotic dehydration process is very effective and efficient. Substantial reduction of the processing time is the most significant improvement in osmotic dehydration. It was confirmed that the water loss and solutes uptake into the carrot tissue mainly occurred during the first 15 to 30 minutes of the process.

The optimum condition was found to be 44% sucrose / 7% NaCl for 16 minutes contact with 26% water loss, 24% mass loss, 2.1% sugar gain and 0.7% NaCl gain. The results revealed that it is important to take into account not only the weight or water loss but also the solid gain in the osmotic treatment. From experimental data, the exponential function was fitted for mass and water reduction, sugar and salt uptake with respect to time.

The phenomenological approach gives an accurate description of the non-linear relationship of the flux to the thermodynamic forces in the diffusional mass transfer of osmotic treatment. Based on quantitative results, it is reasonable to conclude that the model proposed is capable of describing the mass transport phenomena of carrot tissue subject to an osmotic treatment in a sucrose/sodium chloride/water solution. This conclusion is valid because of the high level of agreement between the experimental data and the results predicted.

The application of this model in a parametric study of a continuous osmotic operation gave very satisfactory design parameters for the

dehydration of the carrot cubes from the initial water concentration to a desired final concentration. The validity of the parameters outside these ranges has not been verified.

Osmosis with an alternating sequence of osmotic solution starting with a high NaCl concentration the sucrose/NaCl/water mixture did not show improvement than the constant osmotic solution option.

The present successful result with a continuous osmotic contactor may encourage us to study a greater variety of vegetables or other foods. Since cellular structures and tissue characteristics differ from sample to sample, further studies are needed to investigate the osmotic behavior of other fruit and vegetable materials on the contactor. The data could be processed through the mathematical model developed in this study to determine the required mass transfer parameters.

The recirculation of osmotic solution should be investigated in order to be commercially applicable. The contactor could be extended with a belt type dryer as a processing line for a commercial process. The model can be adopted and modified to determine the size of the osmotic contactor as well.

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8. APPENDIX 1: Average Composition of Carrots and Quality of Products

8.1 Average Composition of Carrots and Nutritional Values

Carrots (*Daucus Carota* L.) are an important and popular vegetable providing fiber and vitamins to the diet. They are extensively used in the food industry. Most of them are in frozen form for use as mixed vegetables and for remanufacture into canned soups. They are also canned (whole, diced or sliced), dehydrated or used in juice manufacture.

The physiological parameters of carrots are abundant in the literature. However, numerous authors have indicated that the chemical composition of carrots vary considerably among carrot varieties, environmental, soil type, harvesting, handling as well as storage conditions (Sistrunk et al, 1967). Sucrose, glucose, fructose and maltose are considered to be the common sugars in carrot (Alabran and Mabrouk, 1973).

According to Belitz and Grosch (1980), the average chemical composition of carrots is given in Table 8.1. The average dry matter content varied from 7.82% to 11.2%. The total sugar content is in the range of 3.46 to 10.74%. Crude fiber is around 1 % and ash is about 0.8% of fresh edible portion.

The mineral composition data are give in Table 8.2. Phosphorus content varied from 22.42 mg/100g to 29.20mg/100g. Iron content, expressed as mg/100g, varied from 2.83 to 3.55. Copper, zinc and

Table 8.1 Average Composition of Carrots
(as % of fresh edible portion).

	Average percent
Dry matter	11.8
N - Compounds	1.1
Carbohydrate	8.7
Lipids	0.2
Crude fiber	1.0
Ash	0.8

Belitz and Grosch (1987).

Table 8.2 Average Mineral Contents of Carrot on a Fresh Weight Basis (mg/100 g)

	Average	Range
Iron	3.19	2.83 - 3.55
Copper	0.17	0.14 - 0.20
Calcium	33.33	30.04 - 36.57
Zinc	0.88	0.70 - 1.06
Manganese	0.21	0.18 - 0.24
Sodium	56.28	53.07 - 59.49
Potassium	277.60	262.12 - 293.08
Phosphorus	25.82	22.42 - 29.20
Ash(%)	0.56	0.53 - 0.59

Bajaj et al. (1980).

manganese content (mg/100g) varied from 0.14 to 0.20, 0.70 to 1.06, and 0.18 to 0.24, respectively. Ash content varied from 0.53% to 0.59%. Sodium and potassium content (mg/100g) varied from 53.07 to 59.49 and 262.12 to 293.08.

8.2 Quality of Osmosed Carrots in NaCl/water Solution

This project is a continuation of the project carried out by Le Maguer and Biswal (1987). In their study, the quality of the osmosed carrots with NaCl-water binary solution was evaluated in terms of textural quality and carotenoids content as well as microbial stability. The study provides information for this continuous process which they were not able to evaluate due to the time limitation. Residual salt content in the carrots is considered as an end-point criterion for the osmotic dehydration. The computer simulation can use the salt content as the cut-off point for dehydration.

The quality attribute of the products were evaluated on carrots treated with NaCl-water solution in boiling water for seven minutes. The residual salt content of reconstituted carrots is less than 2.5% with 15% NaCl solution at 25^{o}C and 60 minutes contact. A taste panel study indicates that the acceptable salt limit lies between 0.037 to 0.46%. It should be noted that the concentration of NaCl in the liquid added to the canned vegetable is about 1.5-2.0% (Joslyn and Timmons, 1967), and salt content of the prepared soup is at 2-2.5% (Watt and Merrill, 1963). Therefore, it is reasonable to assume that the level of salt in the osmotic carrots is acceptable to the consumer.

The study showed carrot cubes osmosed in NaCl-water solution had a softer texture than the fresh ones. The softness of the treated carrots can be attributed ~~to the~~ lytropic effect of NaCl on the tissue (Sterling, 1968)

It is postulated that the pectic substances, as well as other polysaccharides are held together by hydrogen bonds. A lytropic effect refers to the dispersion of the polysaccharide molecules by breaking down hydrogen bonding. Further weakening the tissue by NaCl is also due to the small amount of calcium/sodium ion exchange. Carrots soaked in 15% NaCl solution at 25°C lost half of their calcium content in 30 minutes and two thirds in 60 minutes. Because of calcium removal from the cell, Ca-pectate complexes of middle lamella are destroyed, decreasing the cohesiveness of the cell and resulting in the softening of the tissue. However, this effect is very slight on the texture of the plant tissue.

From the literature, (Speck et al., 1977) it is suggested that a salt treatment is able to stabilize carotenoids. The study showed that conventional air dried products contained only 45 mg carotenoids/100 g dry matter, and salt-treated carrots contained 78 mg /100 g of dry matter after a storage period of 6 months.

Partially dehydrated carrots with NaCl/water solution resulted in microbial stability. It is a progressive decrease in the microbial population in the sample stored at 4°C. Good rehydration ability has been observed.

9 APPENDIX 2. Experimental Data Calculation

9.1 Total Solids Measurement

The total solids measurement was conducted as:

1). Weigh an empty aluminum dish (m_d)

2). Add about 3 - 5 grams of ground carrot in the dish and weigh again ($m_{d+c\ before}$)

3). Dry in vacuum oven at 75°C, 25 Hg mm for 24 hours, after cooling down in a dessicator under vacuum, weigh the dish ($m_{d+c\ after}$)

The total solids (TS) were calculated:

$$TS = \frac{\left[\left[(m_{d+c})_{before} - m_d\right] - \left[(m_{d+c})_{after} - m_d\right]\right]}{\left[(m_{d+c})_{before} - m_d\right]} \qquad [9.1]$$

9.2 Sugar and Sodium Chloride Determination by HPLC

1). A series standard solution of sucrose, glucose, fructose and NaCl were prepared and injected into HPLC system to establish standard curves. A linear regression was obtained between the peak area (PA) and the concentrations respectively.

$$Y = a + b(PA) \qquad [9.2]$$

The examples of standard curves of sucrose, glucose, fructose and NaCl are plotted in Fig. 4.3, Fig. 9.1, Fig. 9.2 and Fig. 9.3 with their regression equations.

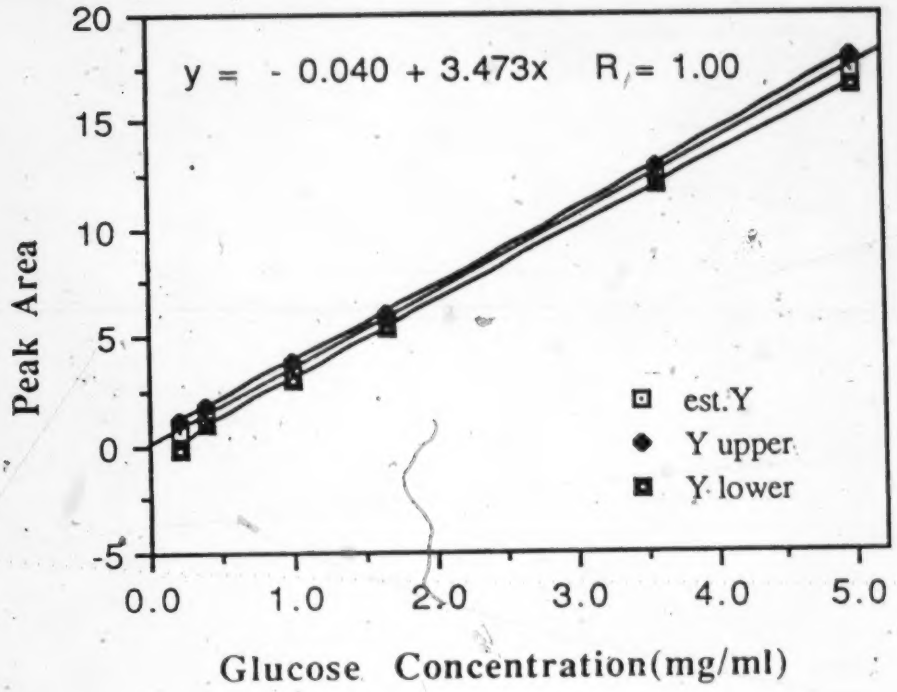

Fig. 9.1 Standard Curve for Glucose

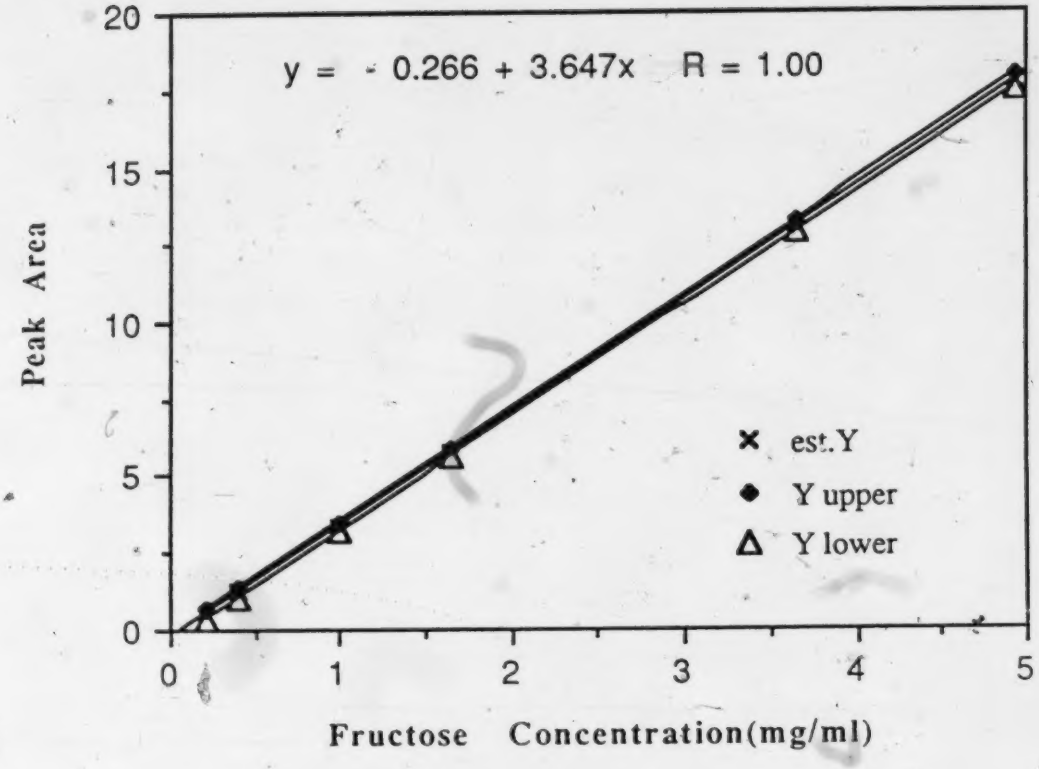

Fig. 9.2 Standard Curve for Fructose

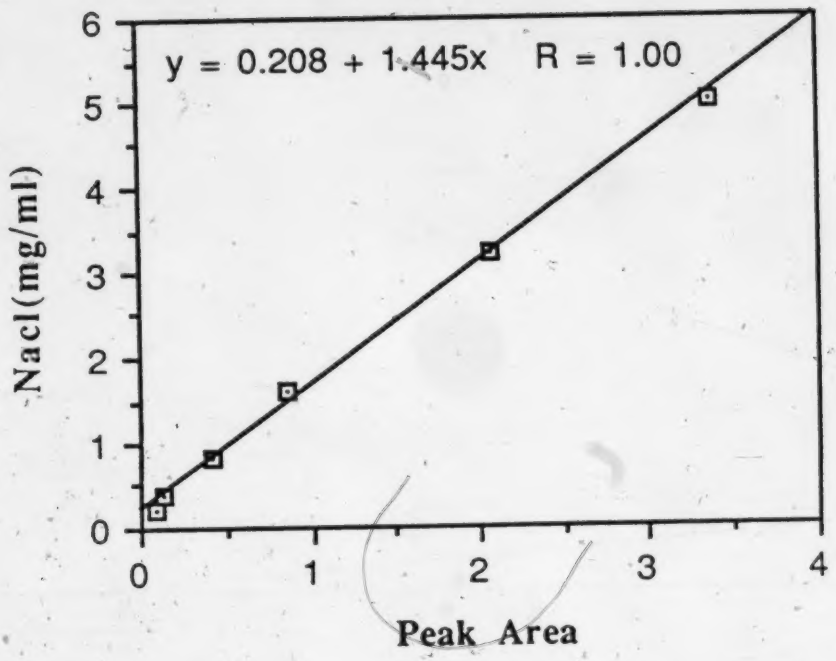

Fig. 9.3 Standard Curve for NaCl

2). The unknown samples were injected into the system and the peak area (PA) was obtained with the Hewlett Packard integrator.

3). The sucrose, glucose, fructose and NaCl are calculated knowing the dilution factor (DF) and the weight of the carrot sample (M_c).

$$SUC \text{ or } SCC = \frac{Y \times DF}{M_c \times 1000} \times 100 \qquad [9.3]$$

9.3 Density Measurement

The volume of the empty pycnometers (V_{py}) were determined by weighing the empty pycnometer (m_{py}), adding distilled water at 23°C and weighing again (m_{py+w}).

$$Vpy = \left[\frac{m_{py+w} - m_{py}}{\rho_{w,23^oC}} \right] \qquad [9.4]$$

The density of samples were performed in the following manner:

1). The empty pycnometer was preweighed (m_{py})

2). Carrot samples were added to the pycnometer and weighed again (m_{py+c})

3). Distilled water at 23°C was added to the pycnometer and weighed again (m_{py+c+w})

The density (ρ) was calculated:

$$\rho = \left[\frac{(m_{py+c} - m_{py})}{V_{py} - \frac{(m_{py+c+m} - m_{py+c})}{\rho_{w,23^oC}}} \right] \qquad [9.5]$$

10 APPENDIX 3. Experimental Measurements of Total Solids (TS), Sugar Content (SUC) and Sodium Chloride Content (SCC) of Carrot Cubes at Different Position Along the Contactor

10.1 TOTAL CONTACT TIME 16 MIN

Solution %	Parameter	Position along contactor 1	2	3	4
30% sucrose 18% NaCl	TS	12.77±0.05	17.34±0.02	19.92±0.12	24.24±0.07
	SUC	6.47±0.39	9.22±0.34	10.38±0.39	12.92±0.41
	SCC	0.22±0.03	2.14±0.13	3.26±0.38	5.41±0.39
30% Sucrose 18% NaCl	TS	12.07±0.01	18.68±0.20	22.18±0.11	24.98±0.34
	SUC	6.51±0.03	9.10±0.43	10.42±0.48	11.34±0.54
	SCC	0.15±0.00	2.96±0.13	4.74±0.33	5.95±1.20
44% Sucrose 7% NaCl	TS	12.95±0.16	15.87±1.58	17.97±1.15	19.77±0.86
	SUC	7.15±0.00	8.34±0.49	10.97±0.40	12.28±0.54
	SCC	0.34±0.24	0.45±0.08	0.98±0.02	1.10±0.14
44% Sucrose 7% NaCl	TS	12.43±0.10	16.30±0.00	18.66±0.18	20.35±0.18
	SUC	6.75±0.13	9.62±0.13	11.76±1.87	12.28±0.82
	SCC	0.27±0.01	0.65±0.04	1.20±0.08	1.55±0.52
47% Sucrose 8% NaCl	TS	13.70±0.16	16.84±2.71	19.36±0.23	22.52±0.08
	SUC	7.50±0.16	9.36±0.68	11.41±0.86	13.93±0.56
	SCC	0.12±0.00	0.54±0.21	1.07±0.15	1.48±0.40
35% Sucrose 22% NaCl	TS	13.24±0.01	19.24±0.02	22.75±0.15	25.95±0.13
	SUC	8.00±0.52	10.63±0.75	12.10±0.75	13.82±1.51
	SCC	0.13±0.00	2.86±0.10	5.65±1.89	6.81±2.67

Note: 1—beginning of the belt 2—the middle of first section
3—the middle of second section 4—the end of the belt

The value reported are average of three replicates ± SD

10.2 Experimental Measurements of Total Solids (TS), Sugar Content (SUC) and Sodium Chloride Content (SCC) of Carrot Cubes at Different Positions Along the Contactor with Different Contact Times

Solution %	Parameter	Position along contactor 1	2	3	4
44% sucrose	TS	12.98±0.14	20.30±0.03	23.59±0.23	26.82±0.24
7% NaCl	SUC	6.63±0.13	9.97±0.11	14.83±2.36	16.56±2.56
C T*: 55(min)	SCC	0.22±0.00	1.10±0.28	1.20±0.10	1.76±0.51
44% Sucrose	TS	12.36±0.02	19.78±0.06	24.28±0.22	27.25±0.19
7% NaCl	SUC	6.26±1:07	10.67±0.98	13.66±1.06	14.49±1.70
C T : 55(min)	SCC	0.20±0.01	1.35±0.14	1.45±0.11	1.67±1.24
47% Sucrose	TS	13.79±0.25	18.96±0.31	25.71±0.03	29.60±0.08
8% NaCl	SUC	8.18±0.27	11.49±0.45	16.56±1.30	18.85±0.72
C T : 60(min)	SCC	0.13±0.00	1.36±0.57	2.89±0.70	2.89±0.80
35% Sucrose	TS	13.24±0.01	27.16±0.11	31.64±0.31	36.41±0.18
22% NaCl	SUC	8.22±0.52	14.85±0.36	15.91±1.06	18.42±0.41
C T : 65(min)	SCC	0.13±0.00	8.32±0.59	10.51±1.86	11.05±1.28

* C T — Contact Time.

11 APPENDIX 4 Experimental Results of M/M_o, M_w/M_o, M_{su}/M_o and M_{sc}/M_o

11.1 M/M_o, M_w/M_o, M_{su}/M_o and M_{sc}/M_o Calculations

As presented previously the calculation of J_i requires the information on M/M_o and M_i/M_o. since insoluble solids in biological materials provide a matrix of tissue which does not change in the osmotic diffusion process, we can express the conservation on total insoluble solids:

$$M\, W_{in} = M_o\, W_{in}^o \qquad [11.1]$$

or

$$\frac{M}{M_o} = \frac{W_{in}^o}{W_{in}} \qquad [11.2]$$

where is W_{in}^o/W_{in} the ratio of weight fraction of insoluble solids initially over the weight fraction of insoluble solids at time t. The ratio of the mass of sucrose,sodium chloride and water in carrot cubes at time t over the mass of carrot cubes initial, M_{su}/M_o, M_{sc}/M_o, Mw/Mo may be expressed as:

$$\frac{M_{su}}{M_o} = \frac{M\, W_{su}}{M_o} = \left[\frac{W_{in}^o}{W_{in}}\right] W_{su} \qquad [11.3]$$

Similarly,

$$\frac{M_{sc}}{M_o} = \frac{M\,W_{sc}}{M_o} = \left[\frac{W^o_{in}}{W_{in}}\right] W_{sc} \qquad [11.4]$$

and

$$\frac{M_w}{M_o} = \frac{M\,W_w}{M_o} = \left[\frac{W^o_{in}}{W_{in}}\right] W_w \qquad [11.5]$$

where W_{sc} is the weight fraction of sodium chloride at time t, W_{su} is the weight fraction of sucrose at time t, W_w is the weight fraction of water at time t.

The process of partial dehydration of plant materials in contact with aqueous solutions of sucrose and sodium chloride is associated with the leaching of soluble solids and uptake of salt and sucrose.

An assumption made throughout the modeling is that the soluble solids do not change during the process. From literature, this assumption may be valid for a short time process, but there may be some soluble solids leaching out for a long processing time. This assumption will be analyzed in the results and discussion section.

Thus, from the conservation of soluble solids

$$\frac{M}{M_o} = \frac{W^o_{in}}{W_{in}} = \frac{W^o_{ss}}{W_{ss}} \qquad [11.6]$$

where W^o_{ss} and W_{ss} are weight fractions of soluble solids initial and at time t.

We have:

$$W_{ss} = \left[\frac{W_{in}}{W^o_{in}} W^o_{ss} \right] \qquad [11.7]$$

From the relation between total solids and the other nonwater elements, one can write:

$$W_{in} + W_{ss} = W_{ts} - W_{su} - W_{sc} \qquad [11.8]$$

Substituting W_{ss} from Eq. [11.7] to Eq. [11.8], thus,

$$W_{in} \left[1 + \frac{W^o_{ss}}{W^o_{in}} \right] = W_{ts} - W_{su} - W_{sc}$$

$$W_{in} = \frac{W_{ts} - W_{su} - W_{sc}}{\left[1 + \frac{W^o_{ss}}{W^o_{in}} \right]} \qquad [11,9]$$

The initial weight fraction of soluble solids can be calculated as:

$$W^o_{ss} = W^o_{ts} - W^o_{su} - W^o_{sc} - W^o_{in} \qquad [11.10]$$

Note: All the quantities with superscript are initial values and without superscript quantities are indicated at time t.

11.2 Experimental

Solution	Time (min)	M/M_o	M_{su}/M_o	M_w/M_o	M_{sc}/M_o
	0.0	1	0.0751	0.8698	0.0012
44% sucrose	5.3	0.8861	0.0852	0.7437	0.0050
7% NaCl	10.6	0.8629	0.0975	0.7292	0.0079
	16.0	0.8114	0.1004	0.6586	0.0081
	18.3	0.8037	0.1049	0.6504	0.0090
	36.0	0.7196	0.1091	0.5461	0.0097
	55.0	0.7026	0.1174	0.5475	0.0101
	0.0	1	0.0750	0.8698	0.0012
47% sucrose	5.3	0.8985	0.0874	0.7282	0.0038
8% NaCl	10.6	0.8436	0.0938	0.7016	0.0068
	16.0	0.7872	0.0991	0.6348	0.0092
	20.0	0.7796	0.1032	0.5998	0.0122
	40.0	0.7096	0.1288	0.5277	0.0163
	60.0	0.6985	0.1317	0.4917	0.0202
	0.0	1	0.0722	0.8698	0.0012
35% sucrose	11.7	0.8345	0.0909	0.6656	0.0239
22% NaCl	21.7	0.8003	0.0961	0.6102	0.0452
	23.3	0.7737	0.0960	0.5652	0.0491
	35.0	0.6708	0.0991	0.4819	0.0527
	43.4	0.6401	0.1069	0.4311	0.0609
	65.0	0.6159	0.1134	0.3855	0.0681
	0.0	1	0.0722	0.8698	0.0012
30% sucrose	5.3	0.9086	0.0744	0.7525	0.0224
18% NaCL	10.6	0.8694	0.0803	0.6875	0.0334
	16.0	0.8488	0.0906	0.6405	0.0472

11.3 Calculated

Solution	Time (min)	M/M_o	M_w/M_o	M_{su}/M_o	M_{sc}/M_o
	0.0	1	0.8698	0.0751	0.0012
44% sucrose	5.3	0.915	0.7761	0.0868	0.0053
7% NaCl	10.6	0.853	0.708	0.0952	0.0075
	16.0	0.808	0.6576	0.1010	0.0087
	18.3	0.793	0.6406	0.1030	0.0090
	36.0	0.726	0.5656	0.1124	0.0092
	55.0	0.703	0.5386	0.1154	0.0100
	0.0	1	0.8698	0.0751	0.0012
47% sucrose	5.3	0.9053	0.7626	0.0850	0.0044
8% NaCl	10.6	0.8399	0.6857	0.0935	0.0071
	16.0	0.7941	0.6297	0.1011	0.0095
	20.0	0.7696	0.5988	0.1059	0.0111
	40.0	0.7126	0.5215	0.1237	0.0168
	60.0	0.6985	0.4994	0.1340	0.0201
	0.0	1	0.8698	0.0751	0.0012
35% sucrose	11.7	0.8555	0.6922	0.0876	0.0283
22% NaCL	21.7	0.7696	0.5802	0.0954	0.0432
	23.3	0.7584	0.5663	0.0979	0.0451
	35.0	0.6919	0.4851	0.1029	0.0557
	43.4	0.6581	0.4446	0.1064	0.0607
	65.0	0.6036	0.3804	0.1123	0.0680
	0.0	1	0.8698	NA	NA
30% sucrose	5.3	0.9093	0.7546	NA	NA
18% NaCl	10.6	0.8683	0.6847	NA	NA
	16.0	0.8495	0.6418	NA	NA

12 APPENDIX 5: Error Propagation on the Experimental Parameters

The propagation error on the calculated parameters such as the mass loss (ML), the water loss (WL), the sugar gain (SUG) and the salt gain (SCG) is presented.

12.1 Error Propagation on the Mass Loss

Recall that:

$$ML = \left[\frac{M}{M_o} - 1 \right] \times 100\% \qquad [12.1]$$

The error on the water loss is calculated as:

$$\frac{\Delta ML}{ML} = \Delta\left(\frac{M}{M_o}\right) \left[\frac{M}{M_o} - 1\right]^{-1}$$

$$= \left[\frac{M_o \Delta M + M \Delta M_o}{M_o^2}\right] \left[\frac{M}{M_o} - 1\right]^{-1} \qquad [12.2]$$

12.2 Error Propagation on the Water Loss

Recall that:

$$WL = \left[\frac{M}{M_o} (1 - W_{ts}) - (1 - W_{ts}^o) \right] \qquad [12.3]$$

The error on water loss is:

$$\frac{\Delta WL}{WL} = \left[\Delta\left(\frac{M}{M_o}\right)+\Delta\left(\frac{M}{M_o}W_{ts}\right)+\Delta W^o_{ts}\right]\left[\frac{M}{M_o}(1-W_{ts})-(1-W^o_{ts})\right]^{-1} \qquad [12.4]$$

12.3 Error Propagation on the Sugar Gain

Recall that:

$$SUG = \left[\frac{M}{M_o}W_{su} - W^o_{su}\right] \qquad [12.5]$$

$$\frac{\Delta SUG}{SUG} = \left[\Delta\left(\frac{M}{M_o}W_{su}\right) + \Delta W^o_{su}\right]\left[\frac{M}{M_o}W_{su} - W^o_{su}\right]^{-1} \qquad [12.6]$$

12.4 Error Propagation on the NaCl Gain

Recall that:

$$SCG = \left[\frac{M}{M_o}W_{sc} - W^o_{sc}\right] \qquad [12.7]$$

The error on the NaCl gain is calculated as:

$$\frac{\Delta SCG}{SCG} = \left[\Delta\left(\frac{M}{M_o}W_{sc}\right) + \Delta W^o_{sc}\right]\left[\frac{M}{M_o}W_{sc} - W^o_{sc}\right]^{-1} \qquad [12.8]$$

The error involved with experimental parameters are standard deviations. The calculated parameters with these propagated errors are used in a Duncan multiple Range Test.